Supporting information for

Efficient 2-Arylbenzothiazole Formation from Aryl Ketones and 2-Aminobenzenethiols under Metal-Free Conditions

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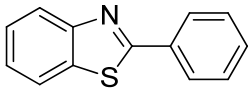
General information:

All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra was measured on Agilent 5975 GC-MS instrument (EI). The structure of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were obtained from commercial suppliers and used without further purification.

General procedure (3a):

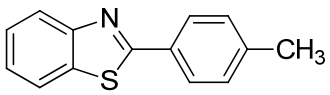
A 10 mL sealed tube was purged with oxygen for three times and was added 2- aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol), acetophenone (**2a**, 58 μL, 0.5 mmol), DMSO (71 μL, 1.0 mmol) and chlorobenzene (2.0 mL) by syringe. The reaction vessel was stirred at 140 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1) to yield the desired product **3a** as white solid (76 mg, 72% yield). Reactions of 2-aminobenzenethiol (**1a**) with propiophenone (**2b**), ethyl 3-oxo-3-phenylpropanoate (**2c**) and benzaldehyde (**2d**) were carried out under similar reaction conditions.

2-Phenylbenzo[*d*]thiazole (3a, CAS: 883-93-2) [1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10-8.07 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.50 (m, 4H), 7.39 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.0, 154.2, 135.1, 133.7, 130.9, 129.0, 127.6, 126.2, 125.1, 123.3, 121.6; MS (EI) *m/z* (%) 211 (100), 184, 108, 82, 69.

2-(p-Tolyl)benzo[*d*]thiazole (3b, CAS: 16112-21-3) [2]

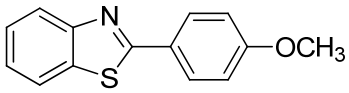


The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(p-tolyl)ethanone (**2e**, 66.8 μL, 0.5 mmol). The residue was purified by column chromatography

on silica gel (petroleum ether/EtOAc = 200:1) afforded the product **3b** as white solid (85.5 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.2, 154.2, 141.3, 135.0, 131.1, 129.7, 127.5, 126.2, 125.0, 123.1, 121.5, 21.4; MS (EI) *m/z* (%) 225 (100), 210, 116, 108, 69.

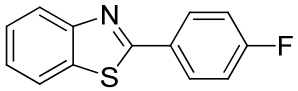
2-(4-Methoxyphenyl)benzo[*d*]thiazole (3c, CAS: 6265-92-5) [3]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(4-methoxyphenyl)ethanone (**2f**, 75 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1) afforded the product **3c** as white solid (74.7 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, J = 8.4 Hz, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 162.0, 154.3, 134.9, 129.1, 126.5, 126.1, 124.7, 122.8, 121.4, 114.4, 55.4; MS (EI) *m/z* (%) 241(100), 226, 198, 154, 69.

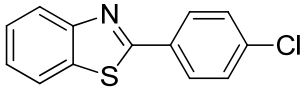
2-(4-Fluorophenyl)benzo[*d*]thiazole (3d, CAS: 6265-92-5) [4]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(4-fluorophenyl)ethanone (**2g**, 60.6 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3d** as white solid (84.7 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11-8.05 (m, 3H), 7.90 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 164.4 (d, J = 250.3 Hz), 154.1, 135.0, 130.0 (d, J = 3.2 Hz), 129.5 (d, J = 8.6 Hz), 126.4, 125.2, 123.2, 121.6, 116.1 (d, J = 22.0 Hz); MS (EI) *m/z* (%) 229 (100), 202, 108, 82, 69.

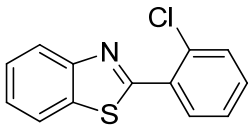
2-(4-Chlorophenyl)benzo[*d*]thiazole (3e, CAS: 6265-91-4) [3]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(4-chlorophenyl)ethanone (**2h**, 65 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3e** as white solid (86 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08-8.02 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.52-7.46 (m, 3H), 7.40 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.6, 154.1, 137.0, 135.1, 132.2, 129.2, 128.7, 126.4, 125.4, 123.3, 121.6; MS (EI) *m/z* (%) 245 (100), 210, 108, 82, 69.

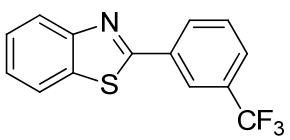
2-(2-Chlorophenyl)benzo[*d*]thiazole (3f, CAS: 6269-46-1) [5]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(2-chlorophenyl)ethanone (**2i**, 67 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) afforded the product **3f** as white solid (79.8 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.23-8.20 (m, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.46-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.1, 152.6, 136.1, 132.7, 132.3, 131.7, 131.0, 130.8, 127.0, 126.2, 125.4, 123.5, 121.3; MS (EI) *m/z* (%) 245 (100), 210, 108, 82, 69.

2-(3-(Trifluoromethyl)phenyl)benzo[*d*]thiazole (3g, CAS: 133389-19-2) [6]

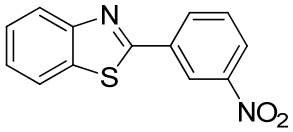


The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and

1-(3-(trifluoromethyl)phenyl)ethanone (**2j**, 76 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3g** as white solid (83.7 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.39 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.0, 154.1, 135.1, 134.5, 131.7 (q, J = 32.5 Hz), 130.7, 129.5, 127.3 (q, J = 3.7 Hz), 126.6, 125.7, 124.3 (q, J = 3.8 Hz), 123.8 (q, J = 270.9 Hz), 123.6, 121.7; MS (EI) *m/z* (%) 279 (100), 260, 108, 82, 69.

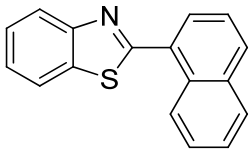
2-(3-Nitrophenyl)benzo[*d*]thiazole (3h, CAS: 22868-33-3) [7]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(3-nitrophenyl)ethanone (**2k**, 82.5 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3h** as white solid (84.5 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.94 (s, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.9, 153.9, 148.7, 135.3, 135.2, 133.0, 130.1, 126.8, 126.0, 125.1, 123.7, 122.3, 121.8; MS (EI) *m/z* (%) 256 (100), 210, 139, 105, 69.

2-(Naphthalen-1-yl)benzo[*d*]thiazole (3i, CAS: 56048-50-1) [8]

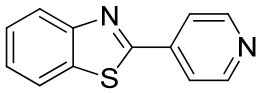


The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(naphthalen-1-yl)ethanone (**2l**, 76 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) afforded the product **3i** as colorless

liquid (88.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.93 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.01-7.93 (m, 4H), 7.64-7.54 (m, 4H), 7.46 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.6, 154.2, 135.5, 134.1, 131.0, 130.9, 130.7, 129.3, 128.4, 127.6, 126.5, 126.2, 125.9, 125.3, 125.0, 123.6, 121.4; MS (EI) *m/z* (%) 261, 260 (100), 130, 116, 69.

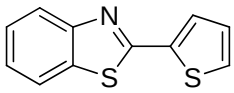
2-(Pyridin-4-yl)benzo[*d*]thiazole (3j, CAS: 2295-38-7) [9]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(pyridin-4-yl)ethanone (**2m**, 55.3 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1) afforded the product **3j** as white solid (58.3 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.78 (d, J = 4.8 Hz, 2H), 8.14 (d, J = 8.0 Hz, 1H), 7.96-7.95 (m, 3H), 7.56 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.1, 154.0, 150.7, 140.5, 135.2, 126.8, 126.2, 123.9, 121.8, 121.2; MS (EI) *m/z* (%) 212 (100), 186, 108, 82, 69.

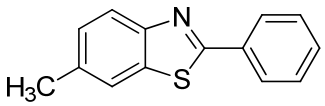
2-(Thiophen-2-yl)benzo[*d*]thiazole (3k, CAS: 34243-38-4) [9]



The reaction was conducted with 2-aminobenzenethiol (**1a**, 96.4 μL, 0.9 mmol) and 1-(thiophen-2-yl)ethanone (**2n**, 54 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3k** as white solid (65.1 mg, 60%).

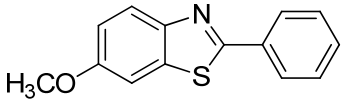
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 3.2 Hz, 1H), 7.51-7.45 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.3, 153.7, 137.4, 134.7, 129.2, 128.5, 128.0, 126.4, 125.2, 123.0, 121.4; MS (EI) *m/z* (%) 217 (100), 173, 108, 82, 69.

6-Methyl-2-phenylbenzo[*d*]thiazole (3l, CAS: 10205-58-0) [5]



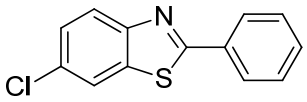
The reaction was conducted with 2-amino-5-methylbenzenethiol (**1b**, 125 mg, 0.9 mmol) and acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) afforded the product **3l** as white solid (83.3 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07 (d, J = 3.6 Hz, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.49-7.48 (m, 3H), 7.30 (d, J = 8.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.0, 152.3, 135.3, 135.2, 133.7, 130.7, 128.9, 127.9, 127.4, 122.7, 121.3, 21.5; MS (EI) *m/z* (%) 225 (100), 209, 121, 77, 69.

6-Methoxy-2-phenylbenzo[*d*]thiazole (3m, CAS: 10205-69-3) [10]



The reaction was conducted with 2-amino-5-methoxybenzenethiol (**1c**, 139.5 mg, 0.9 mmol) and acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3m** as white solid (96.4 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05-8.04 (m, 2H), 7.96 (d, J = 8.8 Hz, 1H), 7.49-7.47 (m, 3H), 7.36 (s, 1H), 7.10 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 157.8, 148.7, 136.4, 133.8, 130.5, 128.9, 127.2, 123.7, 115.6, 104.2, 55.8; MS (EI) *m/z* (%) 241 (100), 226, 198, 95, 69.

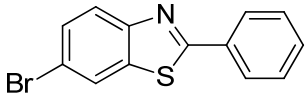
6-Chloro-2-phenylbenzo[*d*]thiazole (3n, CAS: 7466-32-2) [11]



The reaction was conducted with 2-amino-5-chlorobenzenethiol (**1d**, 143.7 mg, 0.9 mmol), acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 500:1) afforded the product **3n** as white solid (85.9 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08-8.07 (m, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.88 (s, 1H), 7.51-7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.5, 152.7, 136.2, 133.2, 131.2, 131.1,

129.1, 127.5, 127.1, 123.9, 121.2; MS (EI) *m/z* (%) 245 (100), 218, 142, 107, 70.

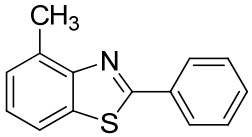
6-Bromo-2-phenylbenzo[*d*]thiazole (3o, CAS: 77333-67-6) [10]



The reaction was conducted with 2-amino-5-bromobenzenethiol (**1e,** 183.6 mg, 0.9 mmol), acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 500:1) afforded the product **3o** as white solid (117.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08-8.05 (m, 3H), 7.92 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.51-7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.5, 153.1, 136.7, 133.3, 131.2, 129.8, 129.1, 127.6, 124.3, 124.1, 118.7; MS (EI) *m/z* (%) 291 (100), 288, 209, 188, 77.

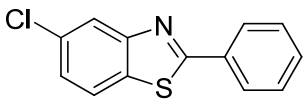
4-Methyl-2-phenylbenzo[*d*]thiazole (3p, CAS: 63325-84-8) [10]



The reaction was conducted with 2-amino-3-methylbenzenethiol (**1f**, 125 mg, 0.9 mmol) and acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200:1) afforded the product **3p** as white solid (62 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12-8.11 (m, 2H), 7.75-7.72 (m, 1H), 7.50-7.49 (m, 3H), 7.29-7.27 (m, 2H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.6, 153.5, 135.0, 134.0, 133.4, 130.7, 128.9, 127.5, 126.8, 125.1, 119.0, 18.4; MS (EI) *m/z* (%) 225 (100), 193, 121, 77, 69.

5-Chloro-2-phenylbenzo[*d*]thiazole (3r, CAS: 952-16-9) [5]

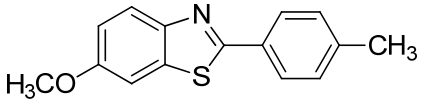


The reaction was conducted with 2-amino-4-chlorobenzenethiol (**1g**, 143.7 mg, 0.9 mmol) and acetophenone (**2a**, 58 μL, 0.5 mmol). The residue was purified by column chromatography on

silica gel (petroleum ether/EtOAc = 50:1) afforded the product **3r** as white solid (86 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09-8.06 (m, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.51-7.50 (m, 3H), 7.37 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 169.9, 155.1, 133.4, 133.4, 132.4, 131.3, 129.1, 127.7, 125.7, 123.1, 122.3; MS (EI) *m/z* (%) 245 (100), 218, 142, 107, 77.

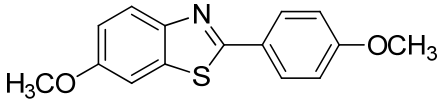
6-Methoxy-2-(p-tolyl)benzo[*d*]thiazole (3s, CAS: 101078-51-7) [12]



The reaction was conducted with 2-amino-5-methoxybenzenethiol (**1c**, 139.5 mg, 0.9 mmol) and 1-(p-tolyl)ethanone (**2e**, 66.8 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) afforded the product **3s** as white solid (97 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (d, J = 8.4 Hz, 3H), 7.35 (s, 1H), 7.27 (t, J = 6.4 Hz, 2H), 7.09 (t, J = 8.8 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.7, 157.6, 148.7, 140.8, 136.2, 131.1, 129.6, 127.1, 123.5, 115.4, 104.1, 55.7, 21.4. MS (EI) *m/z* (%) 255 (100), 240, 212, 95, 69.

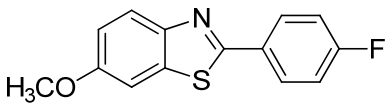
6-Methoxy-2-(4-methoxyphenyl)benzo[*d*]thiazole (3t, CAS: 10205-70-6) [13]



The reaction was conducted with 2-amino-5-methoxybenzenethiol (**1c**, 139.5 mg, 0.9 mmol) and 1-(4-methoxyphenyl)ethanone (**2f**, 75 mg, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3t** as white solid (108.4 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 9.2 Hz, 1H), 7.34 (s, 1H), 7.08-7.06 (m, 1H), 6.99 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.4, 161.6, 157.5, 148.8, 136.2, 128.7, 126.6, 123.3, 115.3, 114.3, 104.3, 55.8, 55.4. MS (EI) *m/z* (%) 271 (100), 256, 228, 213, 95, 70.

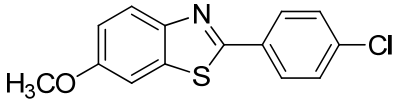
2-(4-Fluorophenyl)-6-methoxybenzo[*d*]thiazole (3u) [13]



The reaction was conducted with 2-amino-5-methoxybenzenethiol (**1c**, 139.5 mg, 0.9 mmol) and 1-(4-fluorophenyl)ethanone (**2g**, 60.6 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) afforded the product **3u** as white solid (91 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05-8.01 (m, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 7.17 (t, J = 8.6 Hz, 2H), 7.10 (d, J = 6.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.2, 164.1(d, J = 249.7 Hz), 157.8, 148.6, 136.4, 130.1 (d, J = 3.4 Hz), 129.1 (d, J = 8.6 Hz,), 123.6, 116.0 (d, J = 21.9 Hz), 115.7, 104.2, 55.8. MS (EI) *m/z* (%) 259 (100), 244, 216, 95, 69.

2-(4-Chlorophenyl)-6-methoxybenzo[*d*]thiazole (3v, CAS: 92161-47-2) [13]



The reaction was conducted with 2-amino-5-methoxybenzenethiol (**1c**, 139.5 mg, 0.9 mmol) and 1-(4-chlorophenyl)ethanone (**2h**, 65 μL, 0.5 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) afforded the product **3v** as white solid (93.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99-7.93 (m, 3H), 7.45 (d, J = 8.4 Hz, 2H), 7.35 (s, 1H), 7.11-7.09 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.0, 158.0, 148.7, 136.5, 136.5, 132.3, 129.2, 128.4, 123.8, 115.8, 104.2, 55.8. MS (EI) *m/z* (%) 275 (100), 260, 232, 95, 69.

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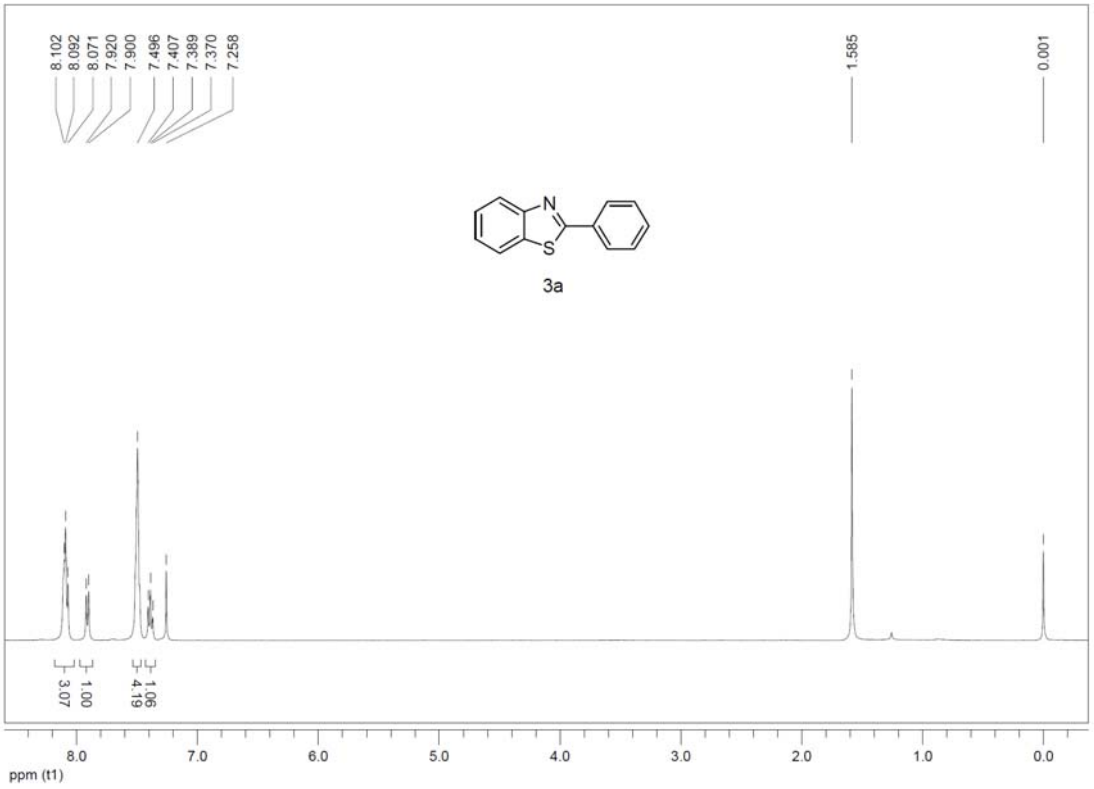
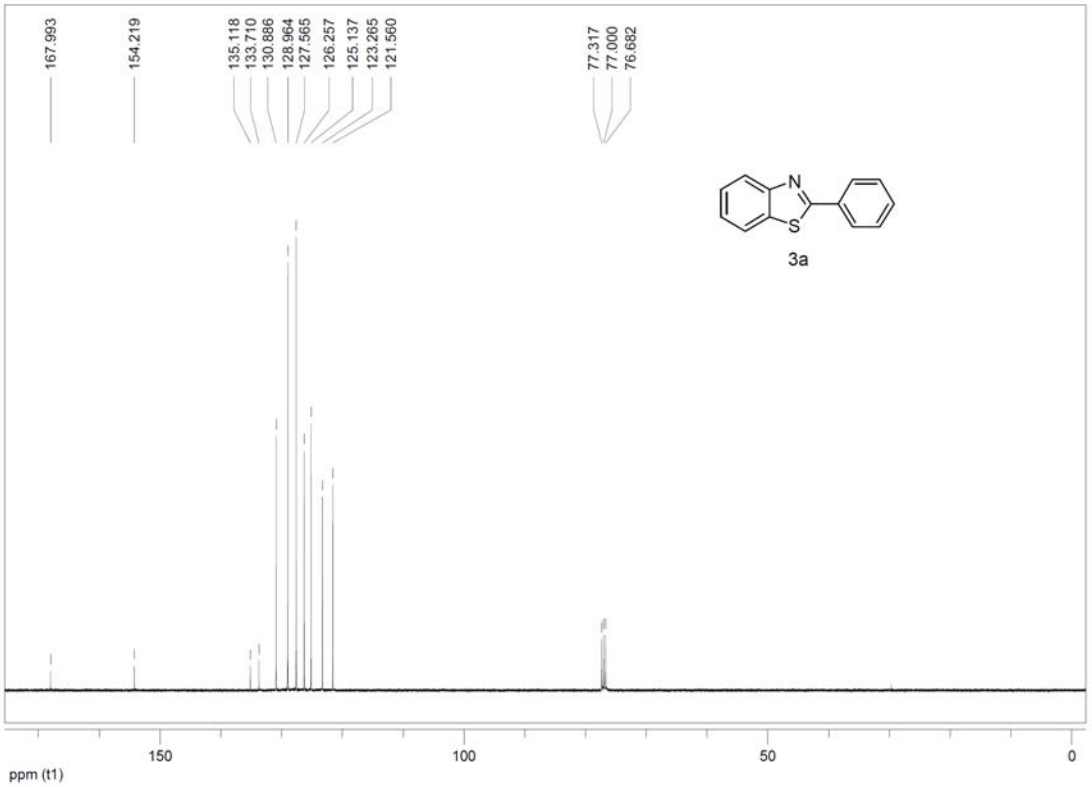
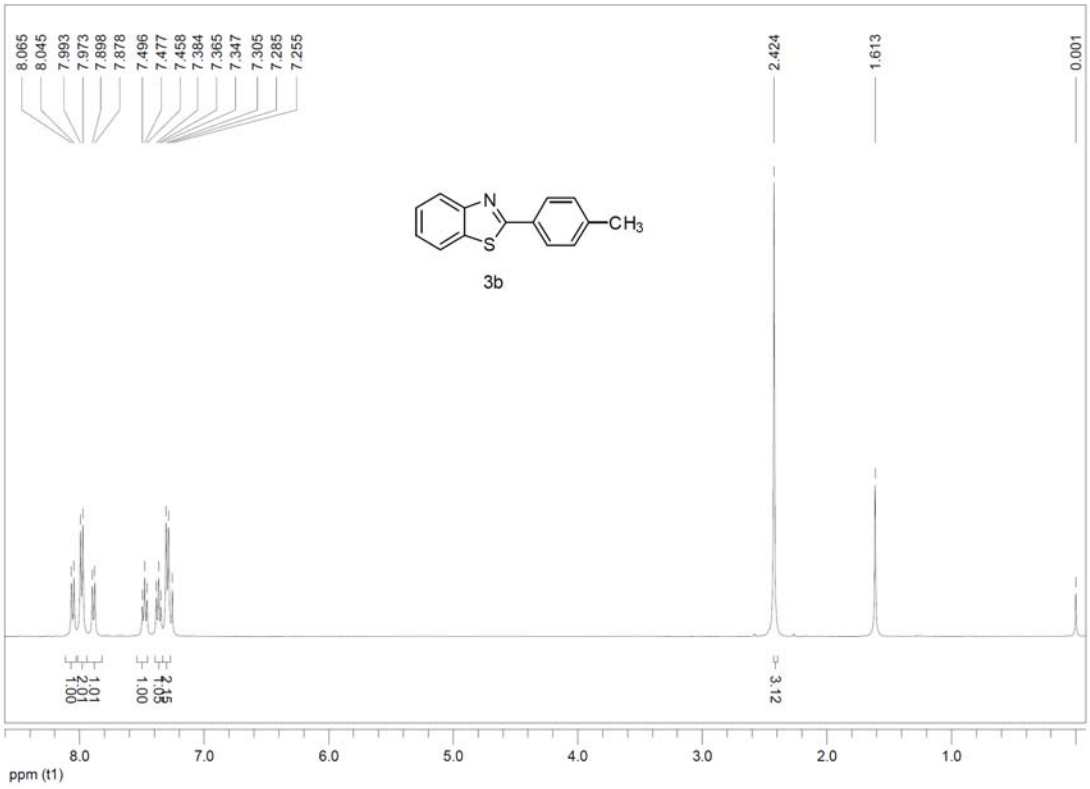
^{1}H NMR and ^{13}C NMR spectra



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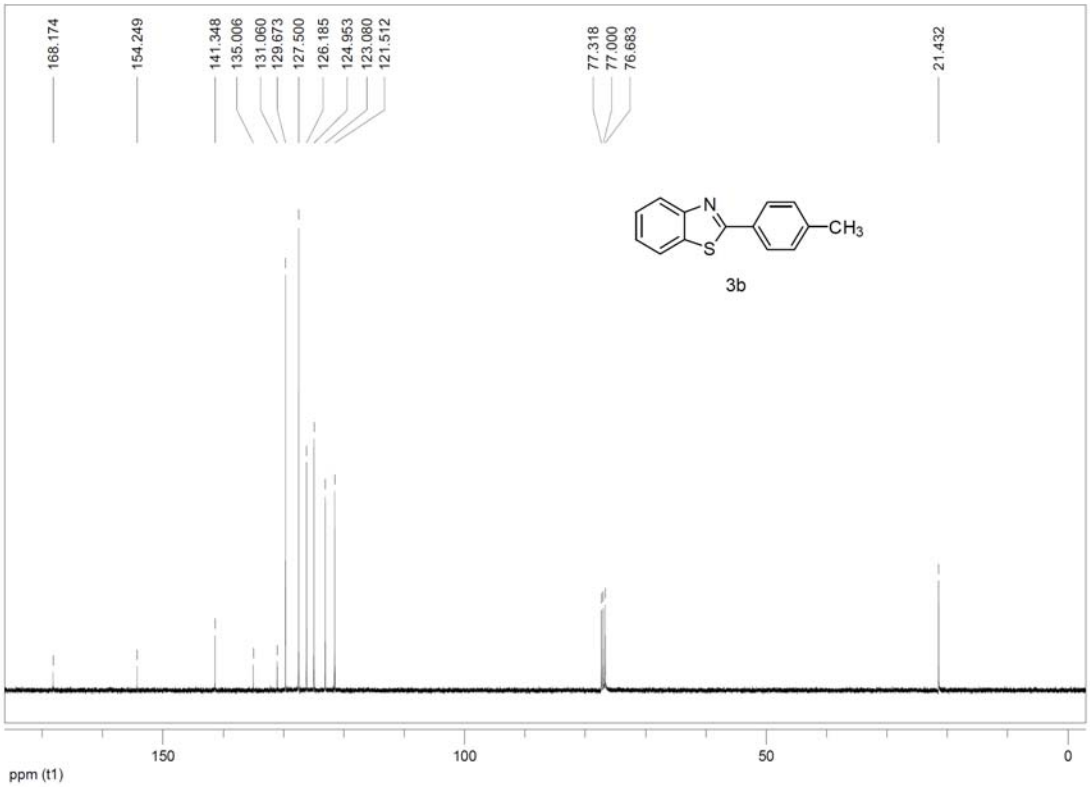
7.973
7.898
7.878
7.496
7.477
7.458
7.384
7.365
7.347
7.305
7.285
7.255
2.424
1.613
0.001
3b
1.00
2.11
1.01
1.00
2.15
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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129.673
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77.000
76.683
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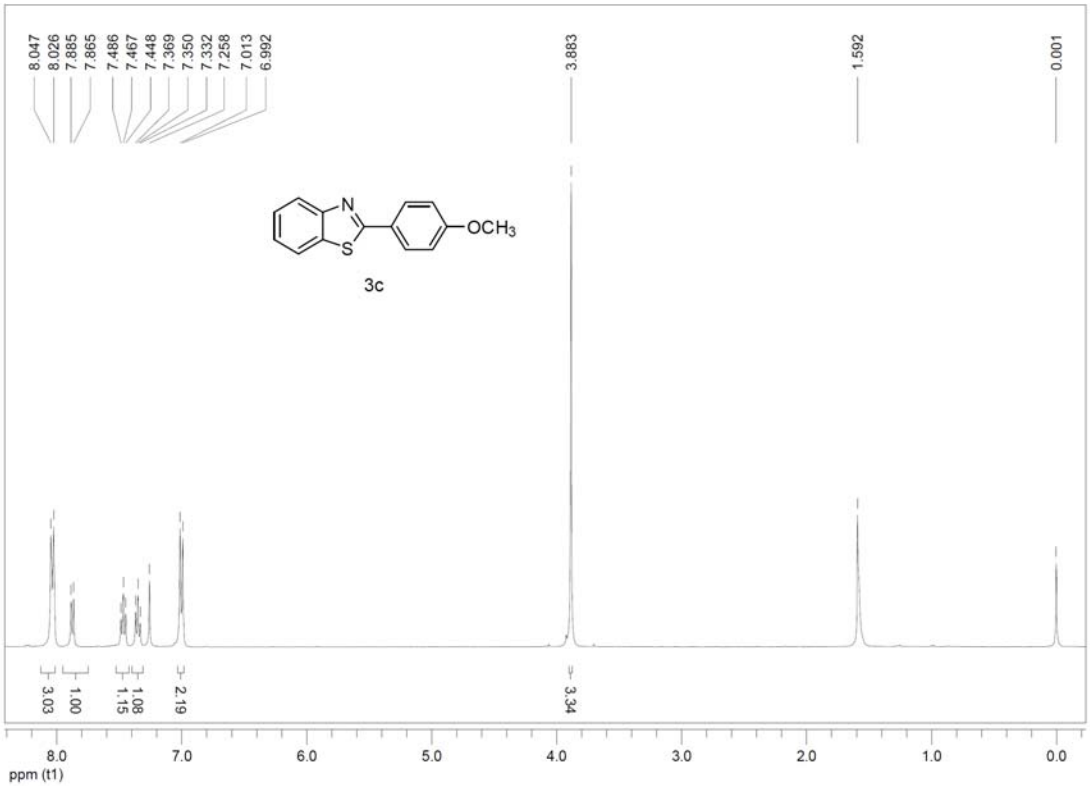
50
0
ppm (t1)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7.885
7.865
7.486
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7.448
7.369
7.350
7.332
7.258
7.013
6.992
3.883
1.592
0.001
OCH3
3c
3.03
1.00
1.15
1.08
2.19
3.34
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7.0
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5.0
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2.0
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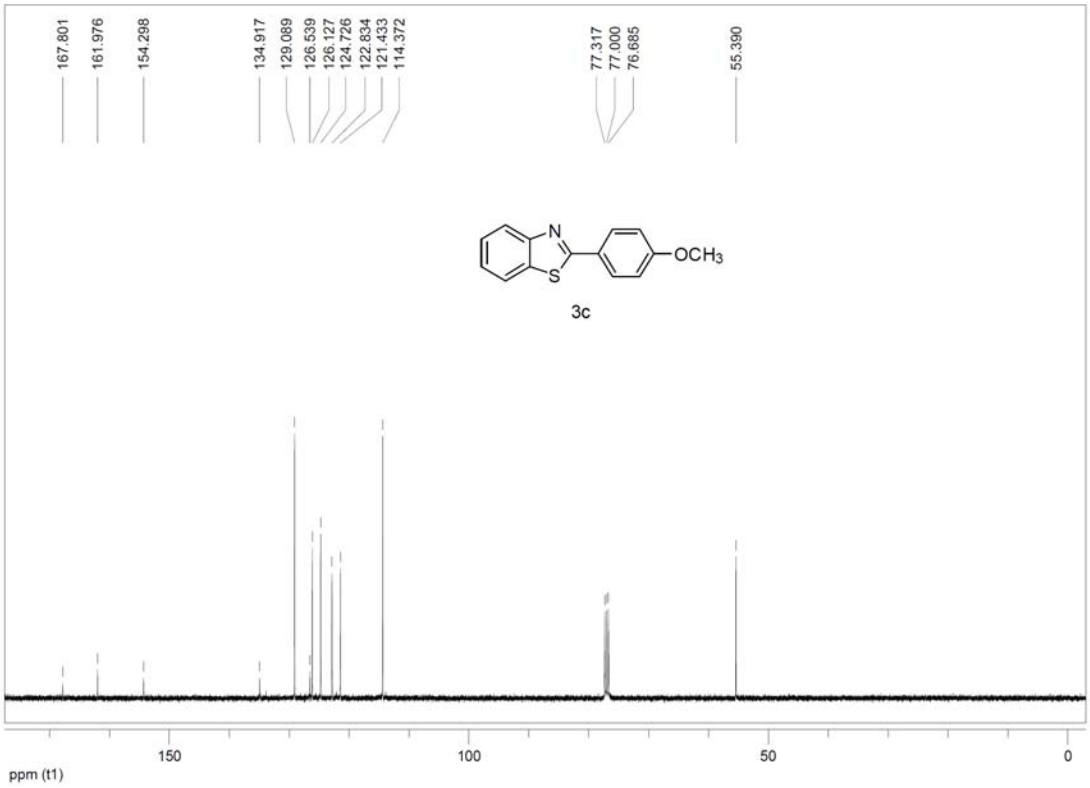
ppm (t1)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154.298
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122.834
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77.000
76.685
55.390
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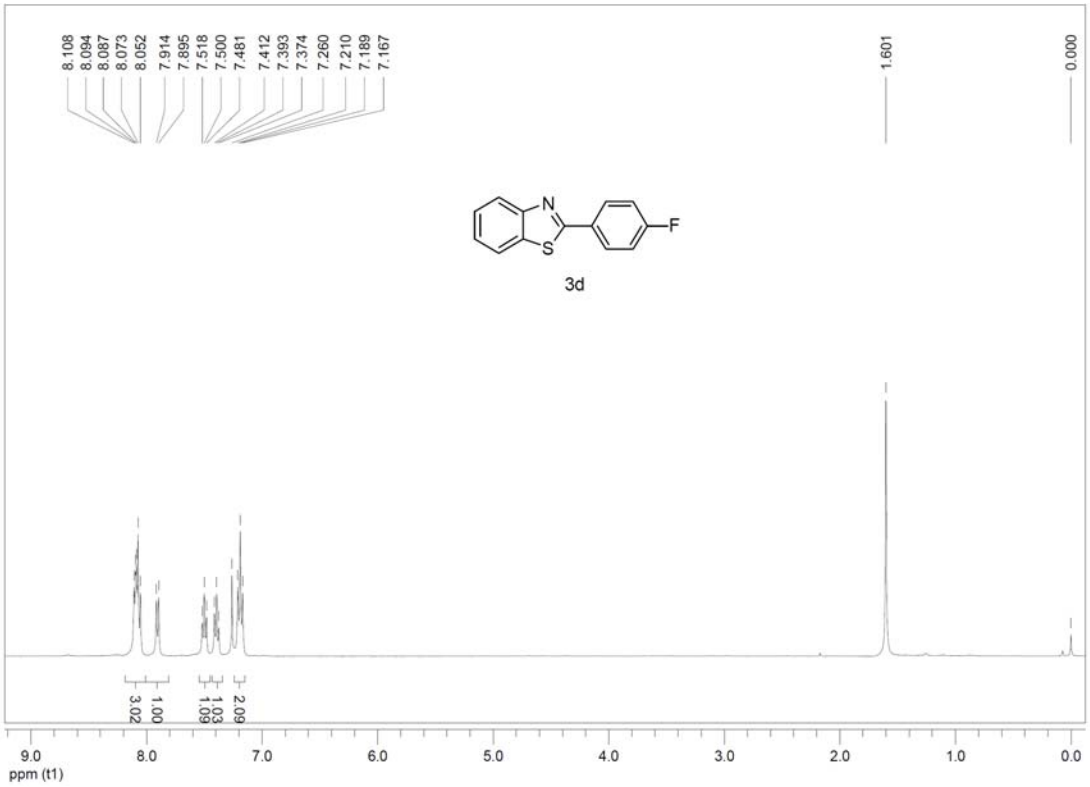
50
0
ppm (t1)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7.374
7.260
7.210
7.189
7.167
1.601
0.000
3d
3.02
1.00
1.09
1.03
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5.0
4.0
3.0
2.0
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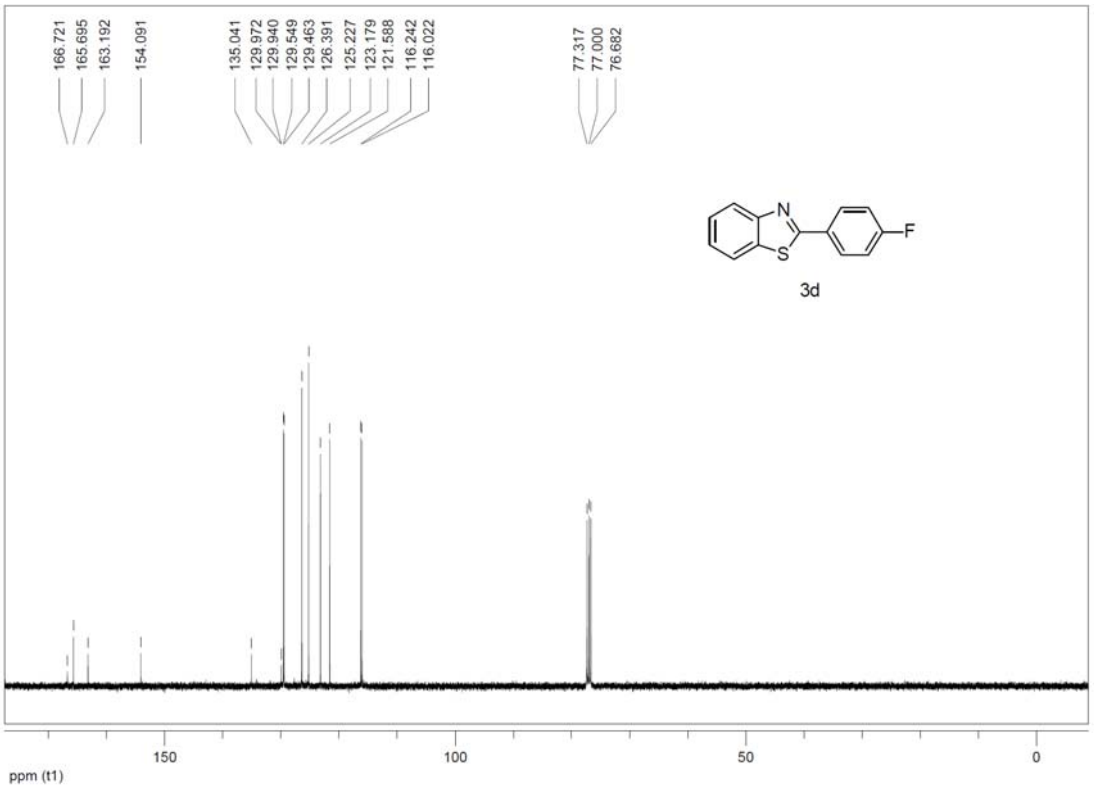
0.0
ppm (t1)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116.242
116.022
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77.000
76.682
3d
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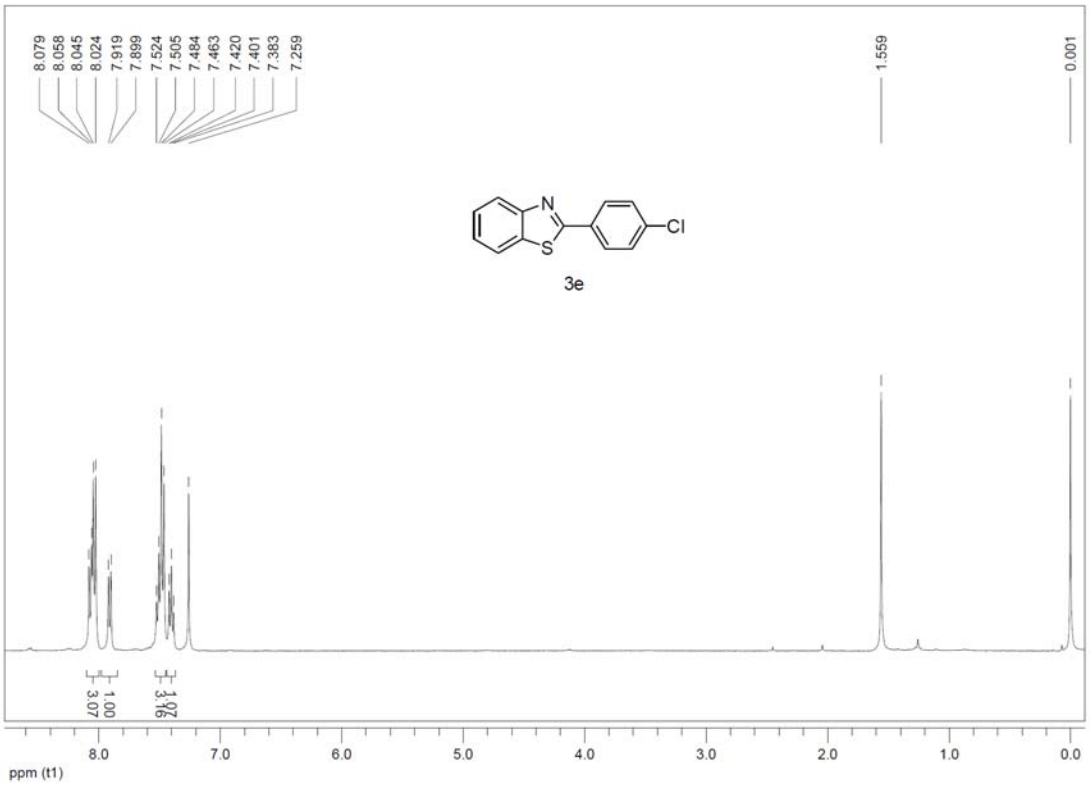
100
50
0
ppm (t1)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7.524
7.505
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7.463
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7.401
7.383
7.259
1.559
0.001
N
S
Cl
3e
3.07
1.00
3.16
3.02
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7.0
6.0
5.0
4.0
3.0
2.0
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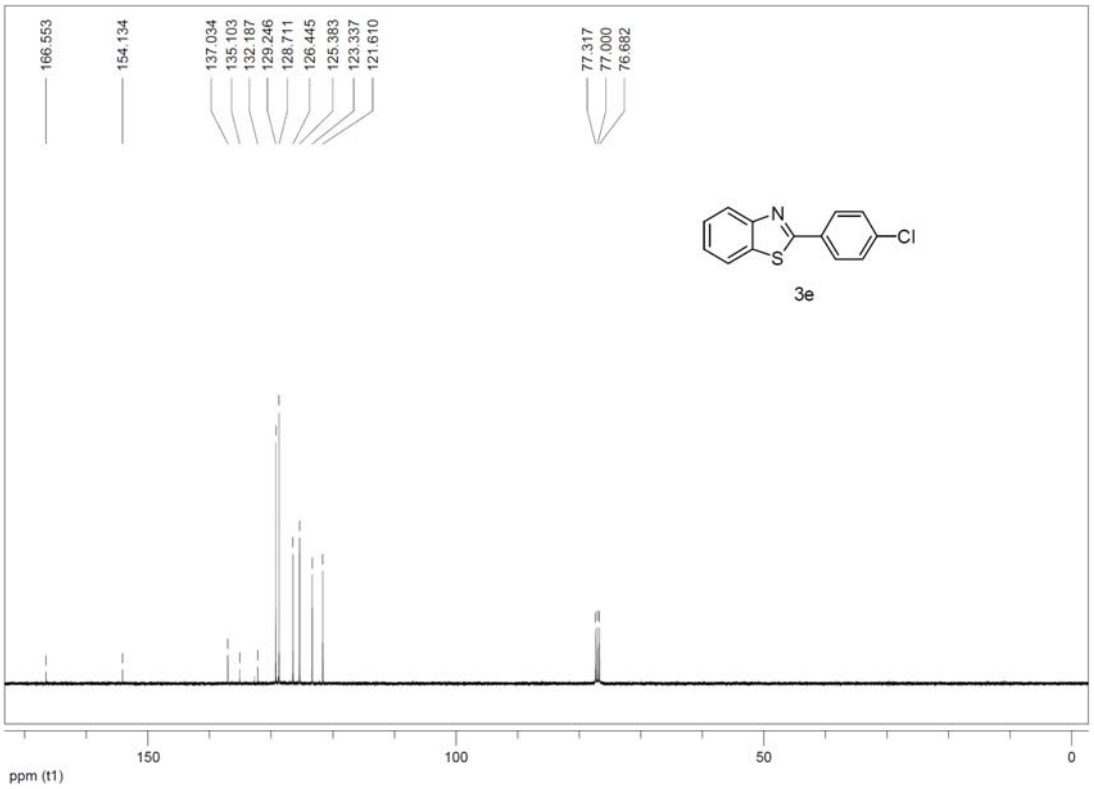
0.0
ppm (t1)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77.000
76.682
N
S
Cl
3e
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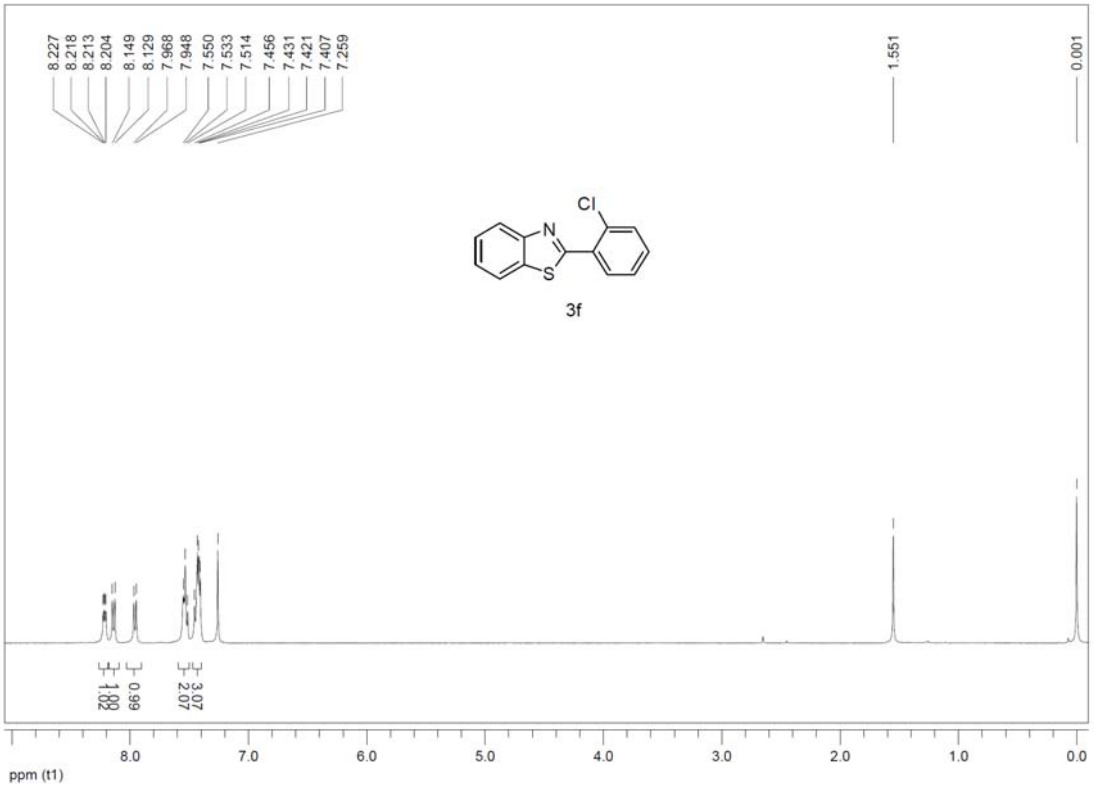
100
50
0
ppm (t1)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7.431
7.421
7.407
7.259
1.551
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Cl
N
S
3f
1.02
0.99
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5.0
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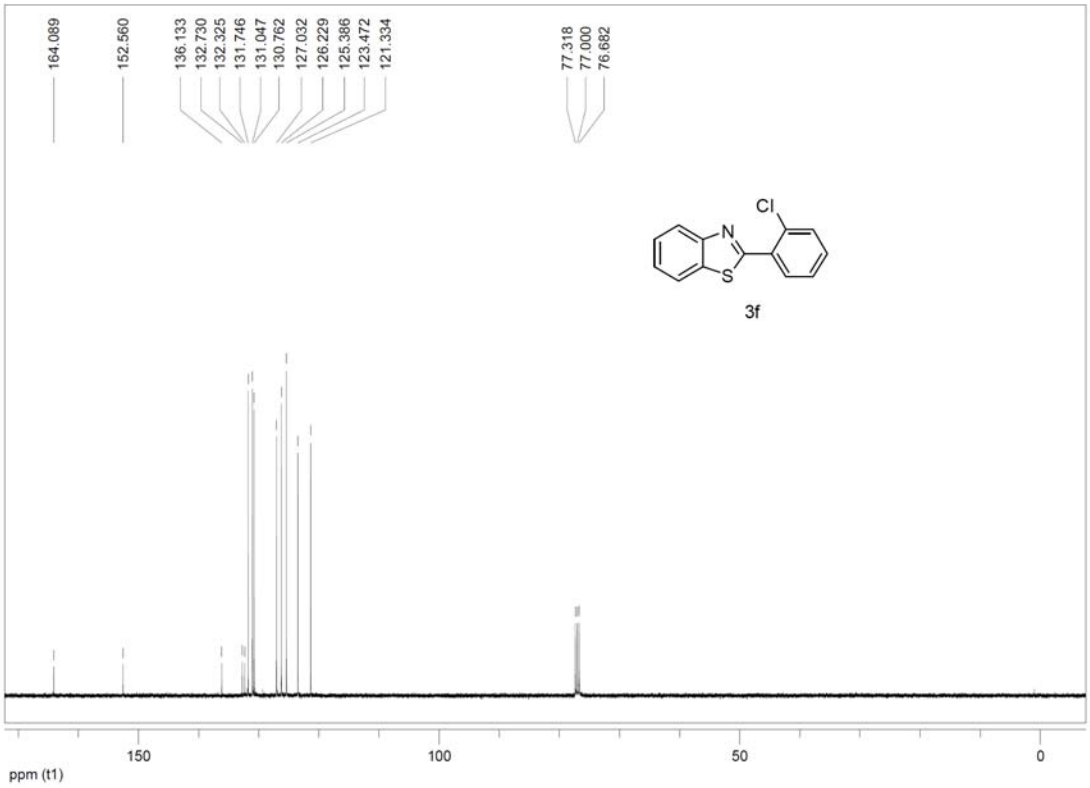
0.0
ppm (t1)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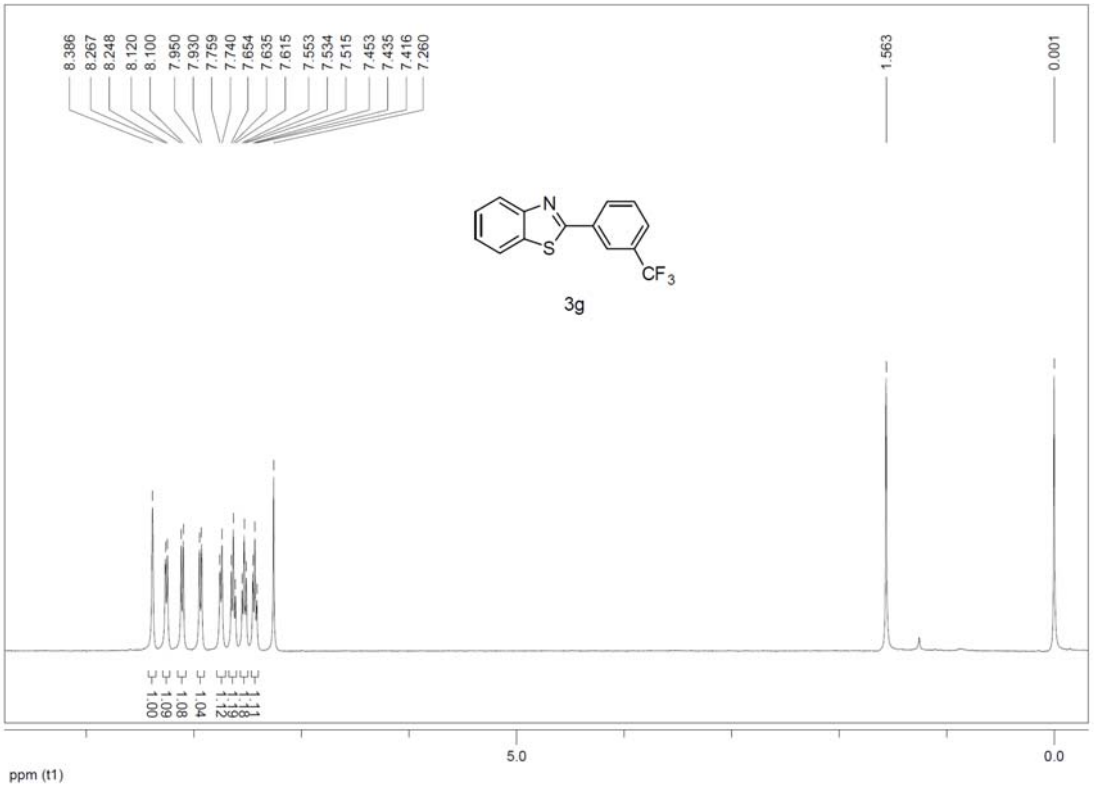
0
ppm (t1)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7.534
7.515
7.453
7.435
7.416
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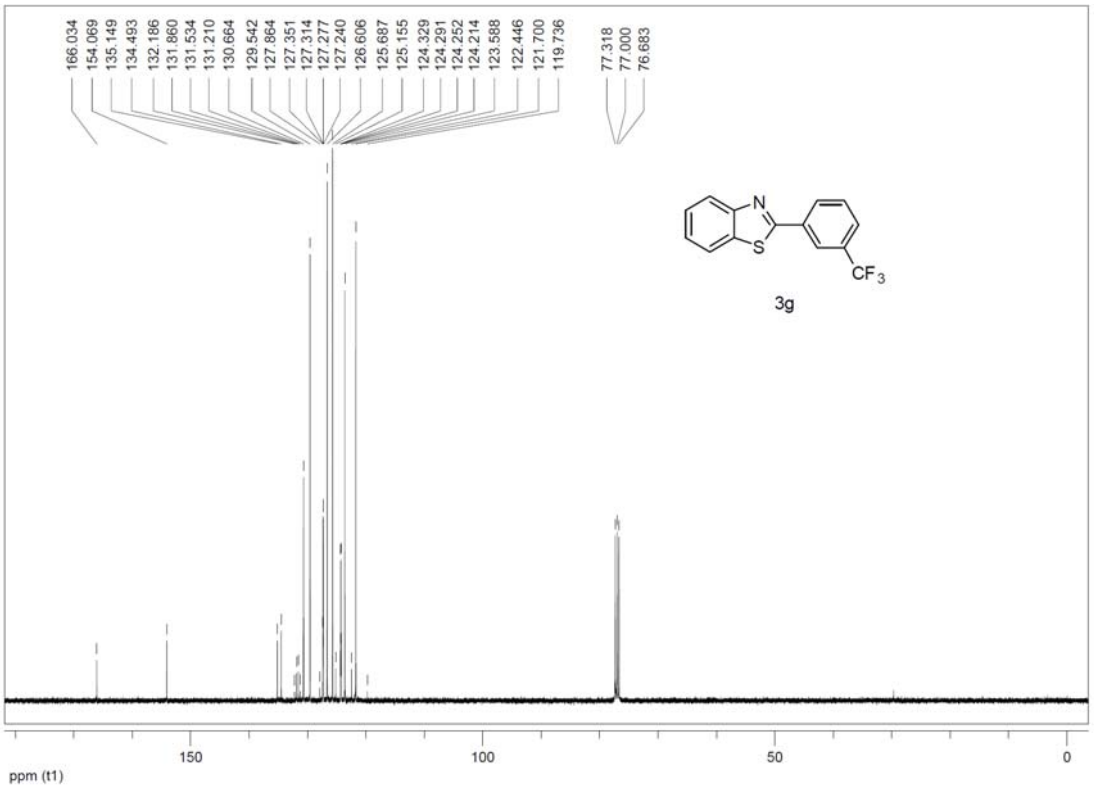
ppm (t1)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125.155
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124.252
124.214
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50
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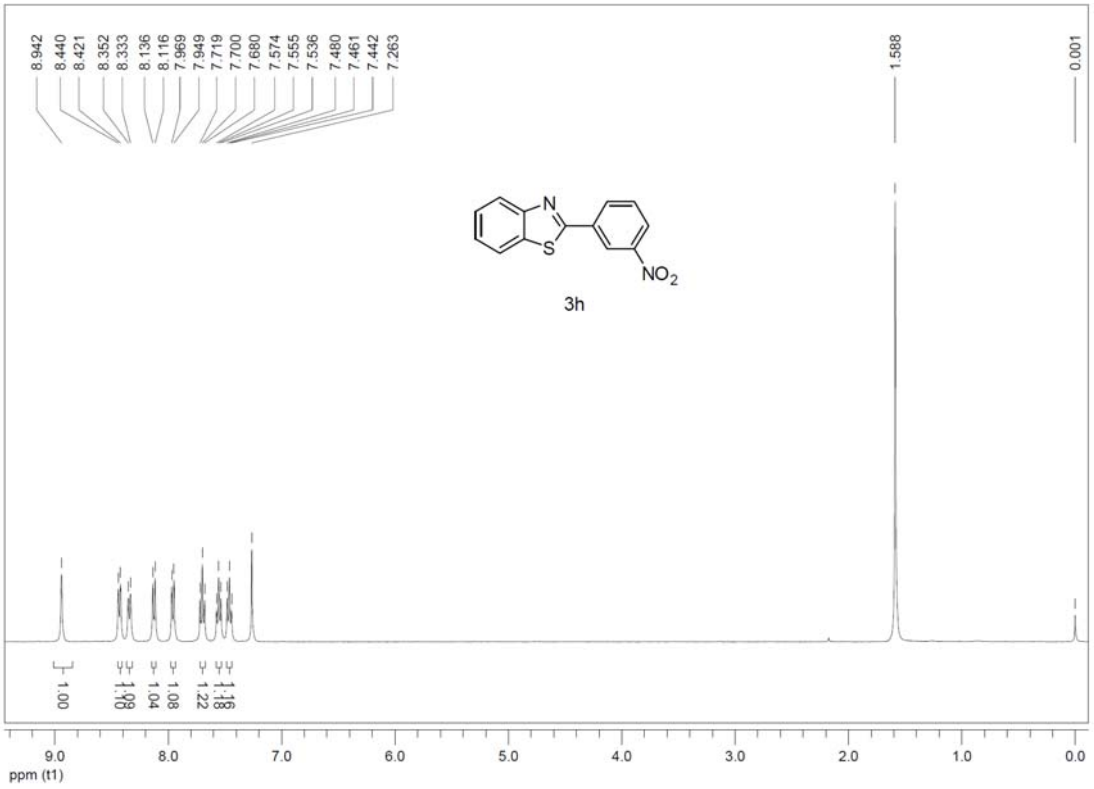
ppm (t1)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7.949
7.719
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7.680
7.574
7.555
7.536
7.480
7.461
7.442
7.263
1.588
0.001
N
S
NO2
3h
1.00
2.10
2.08
1.04
1.08
1.22
1.18
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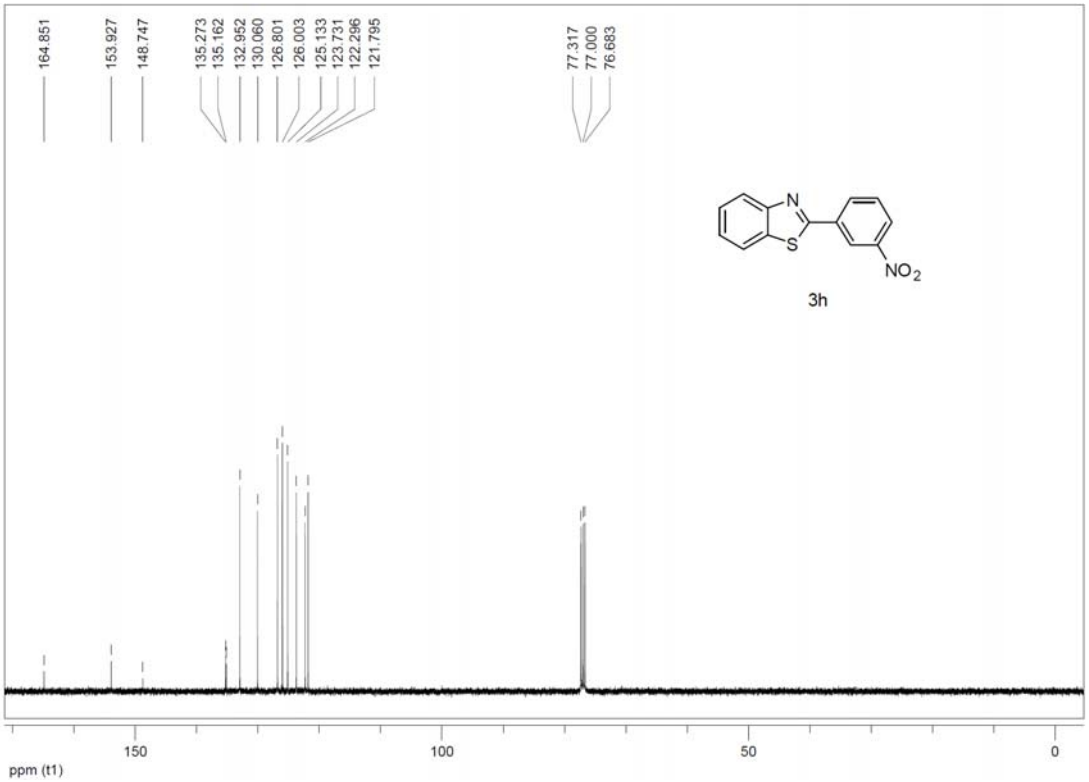
ppm (t1)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125.133
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S
NO2
3h
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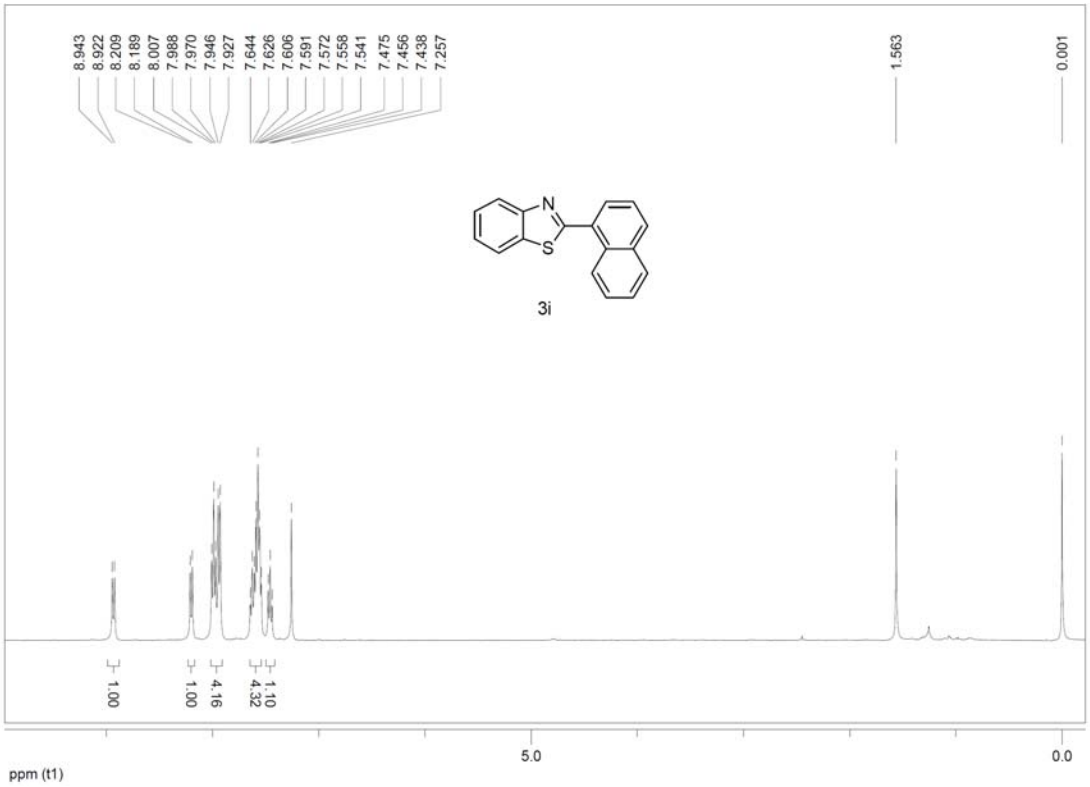
50
0
ppm (t1)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7.558
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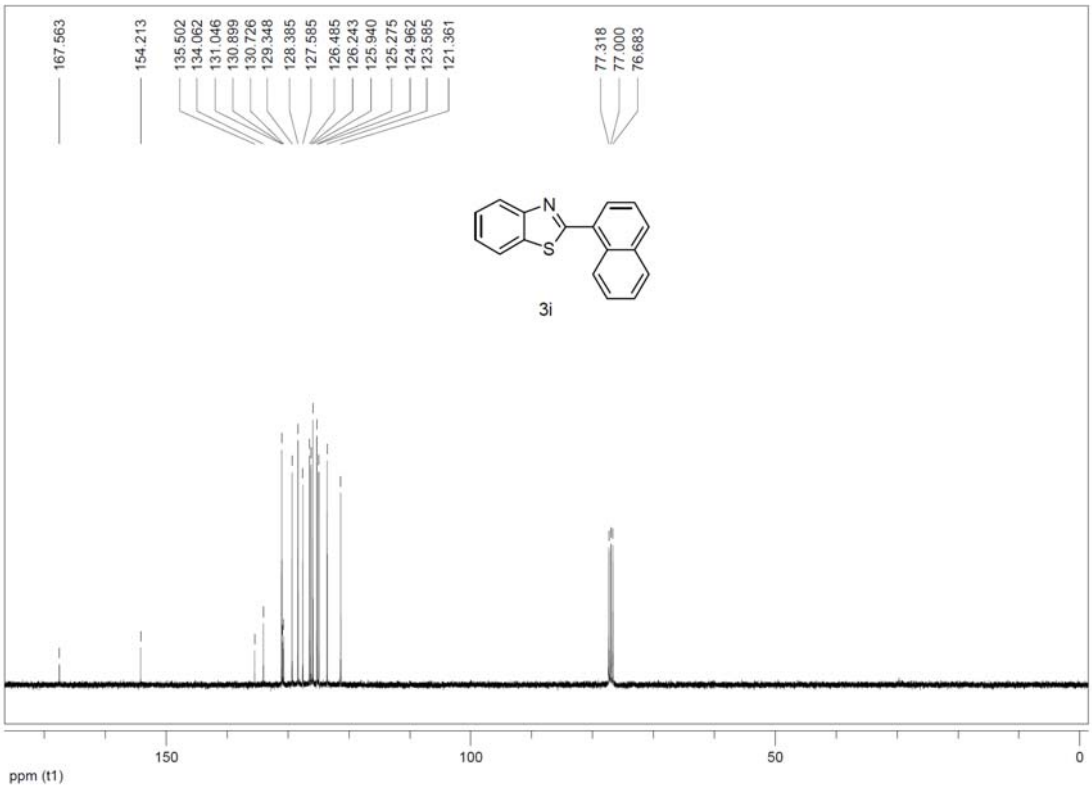
ppm (t1)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123.585
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77.000
76.683
3i
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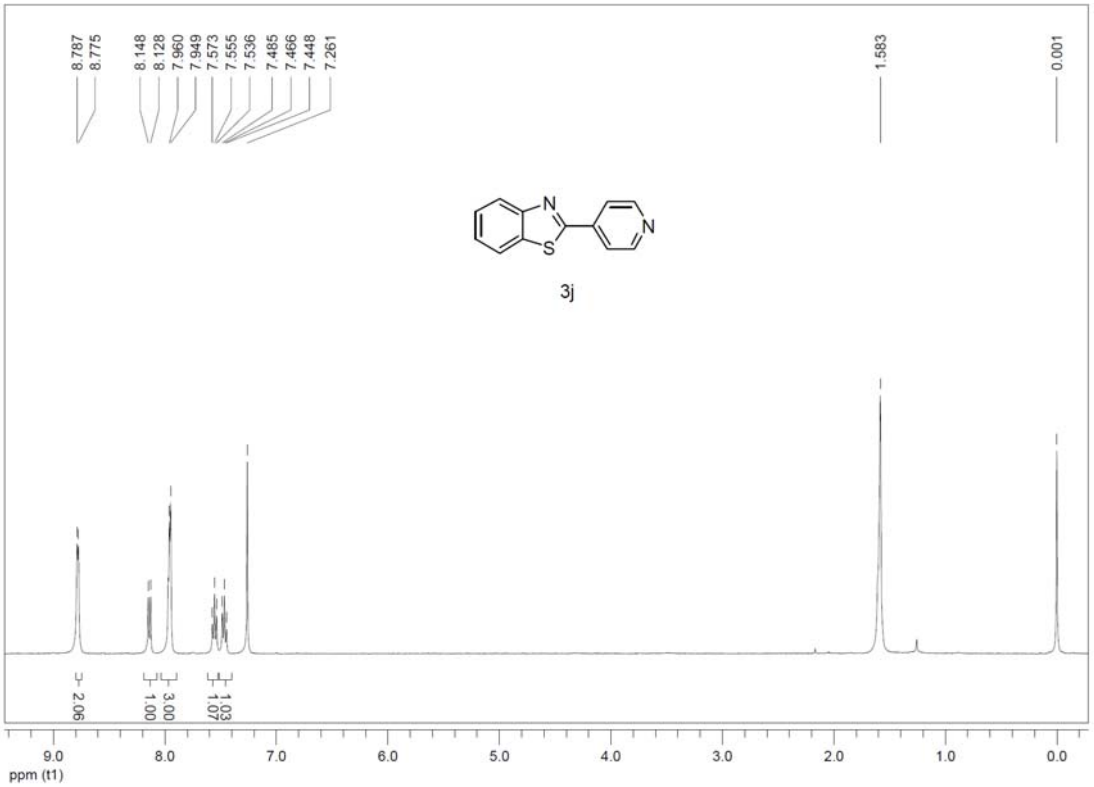
50
0
ppm (t1)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3j
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1.00
3.00
1.07
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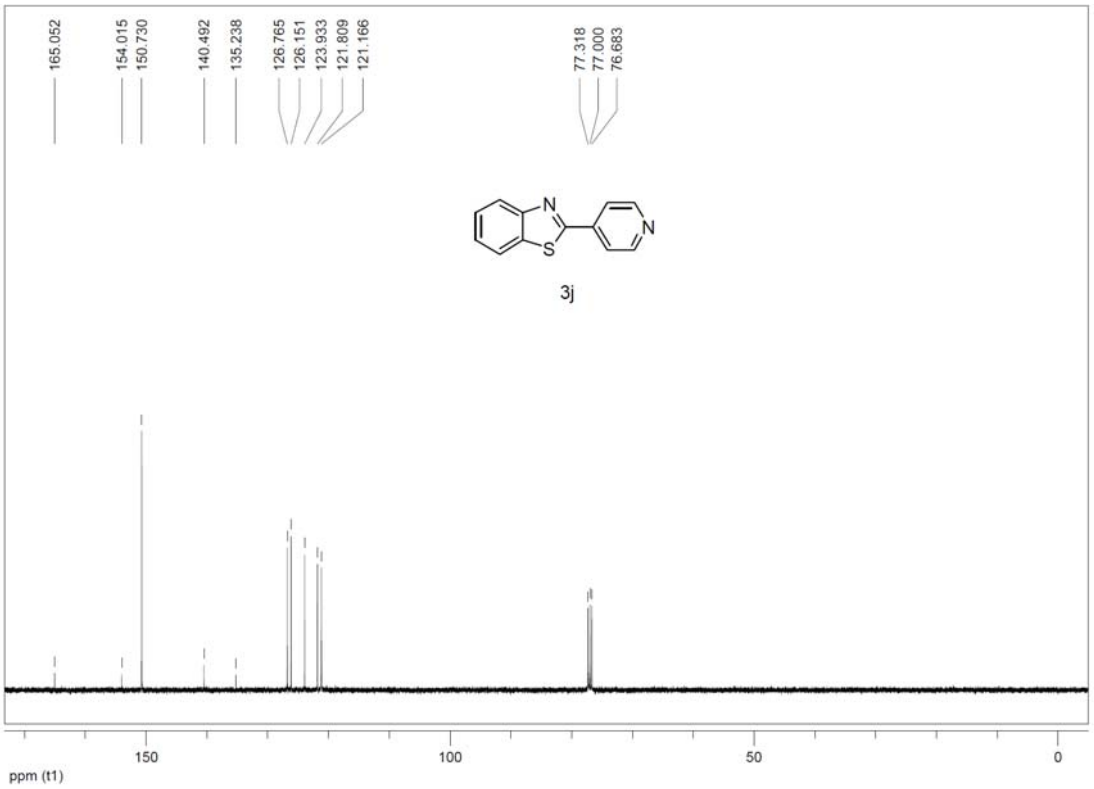
ppm (t1)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77.000
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3j
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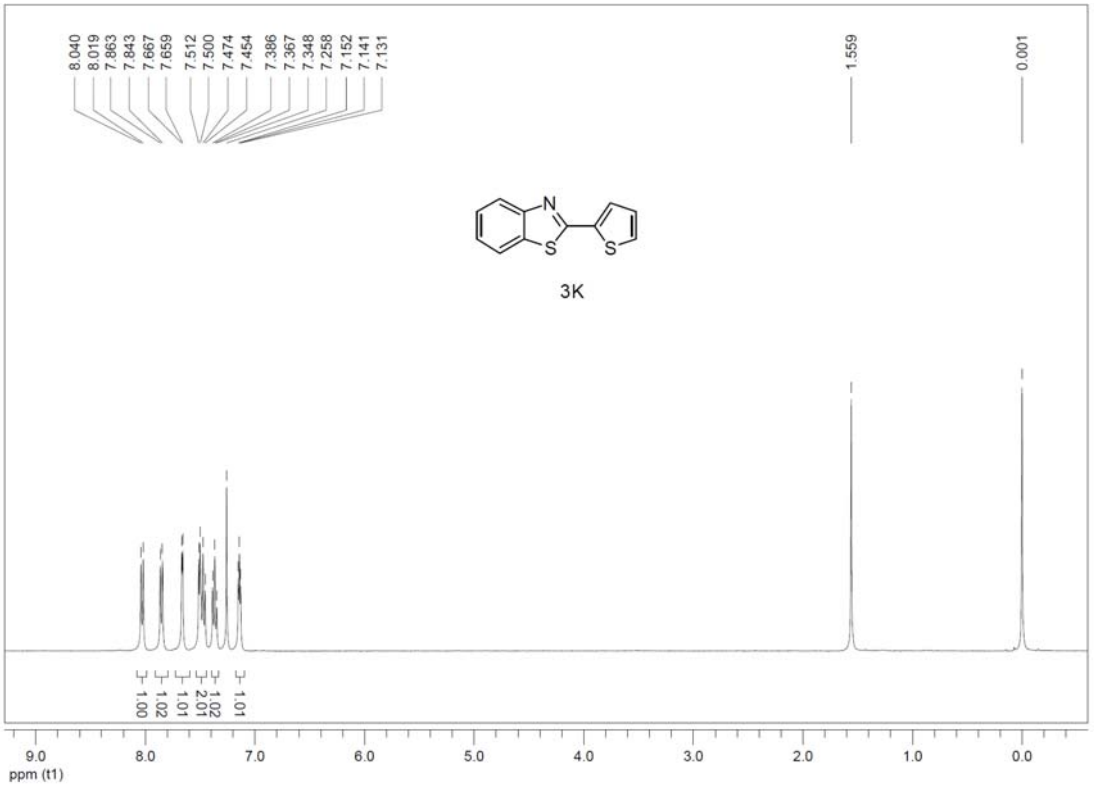
100
50
0
ppm (t1)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1.02
1.01
2.01
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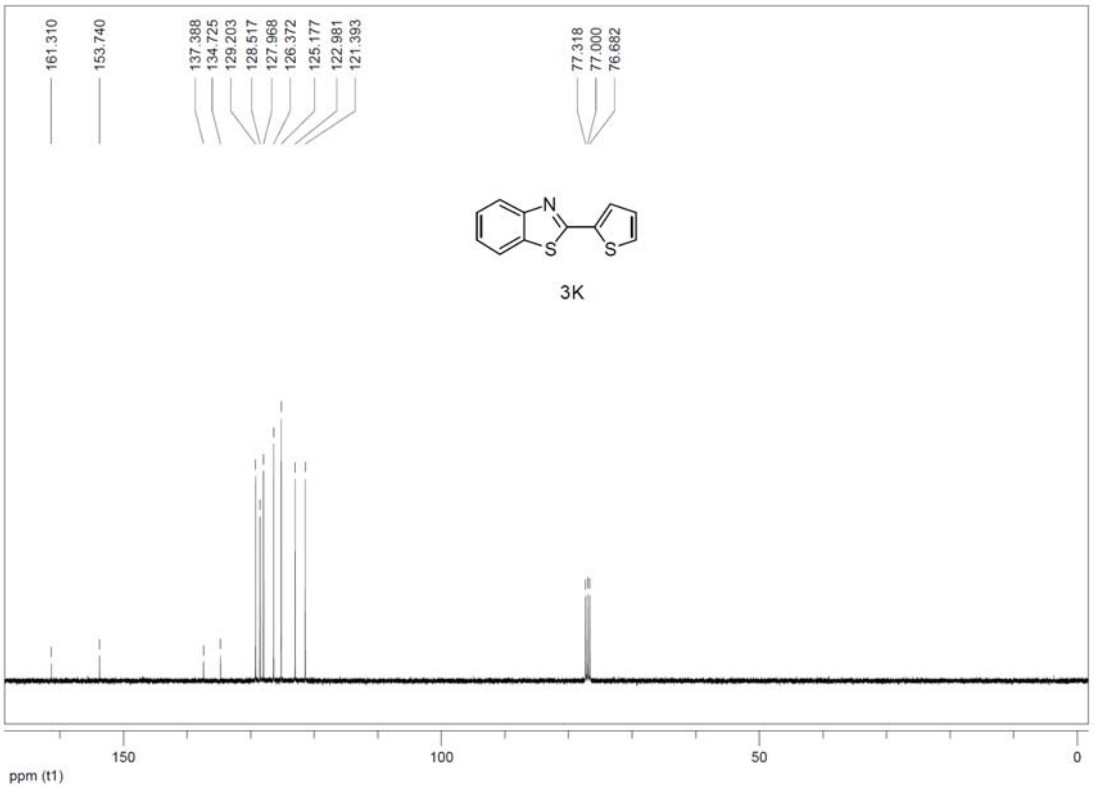
ppm (t1)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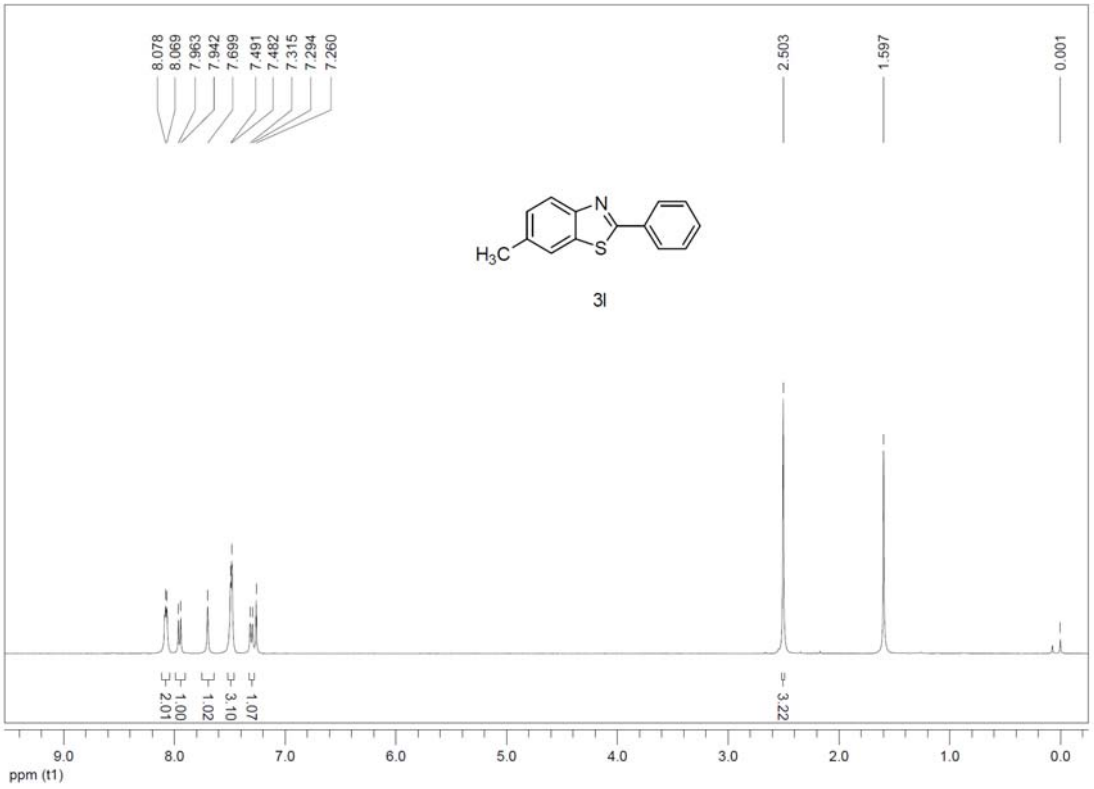
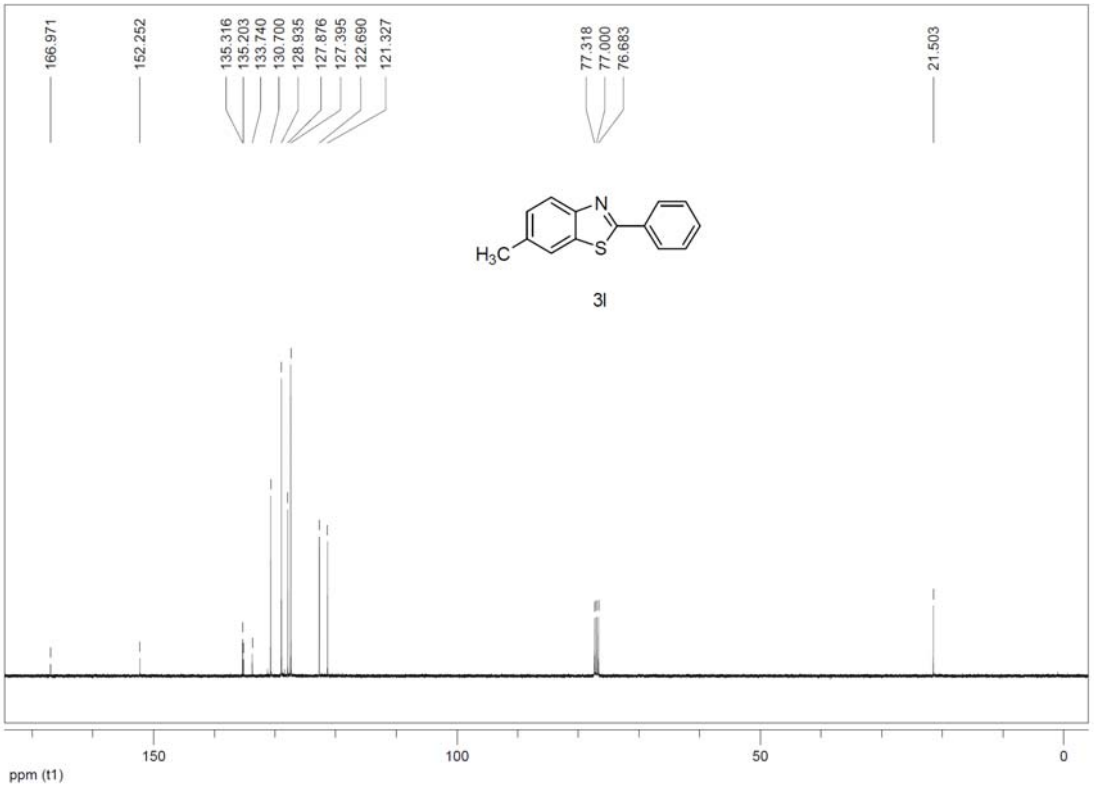
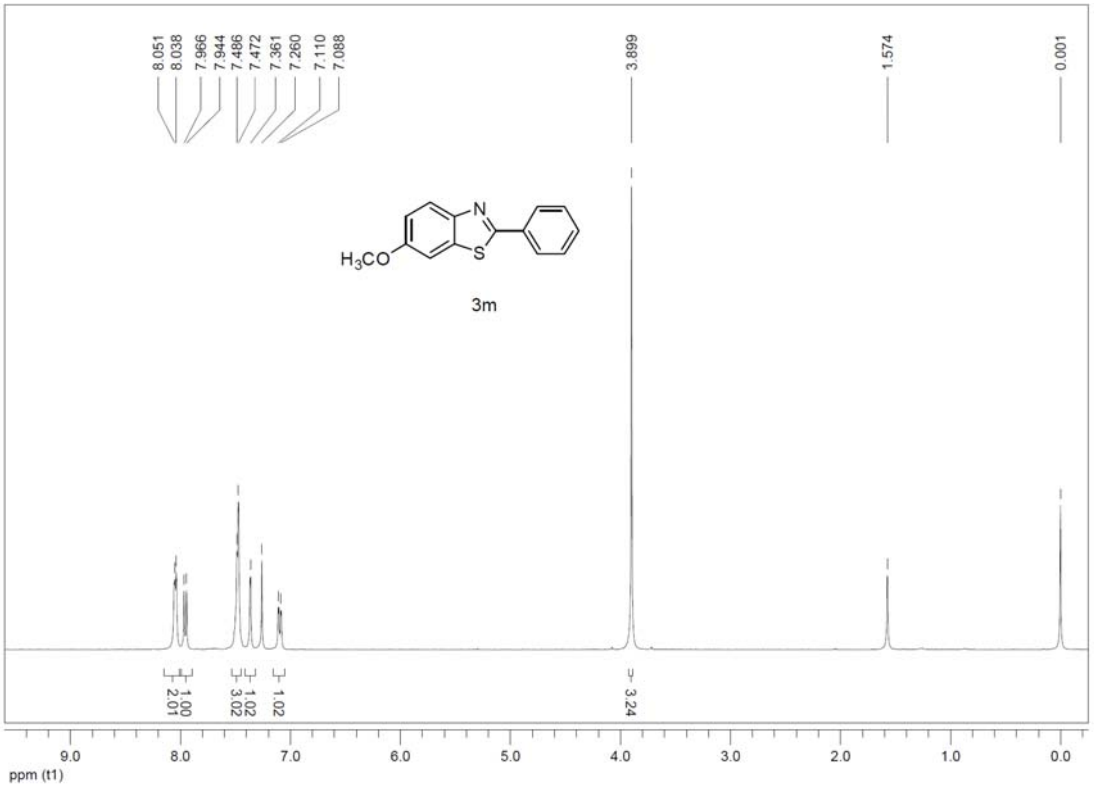
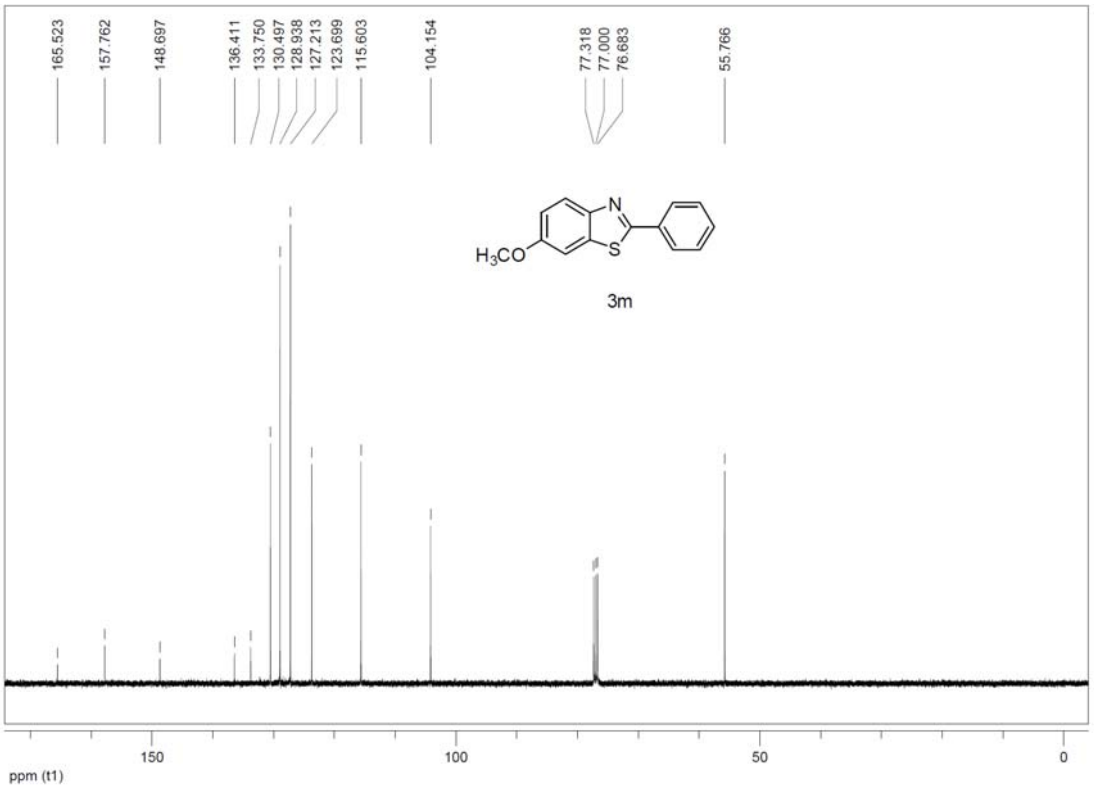
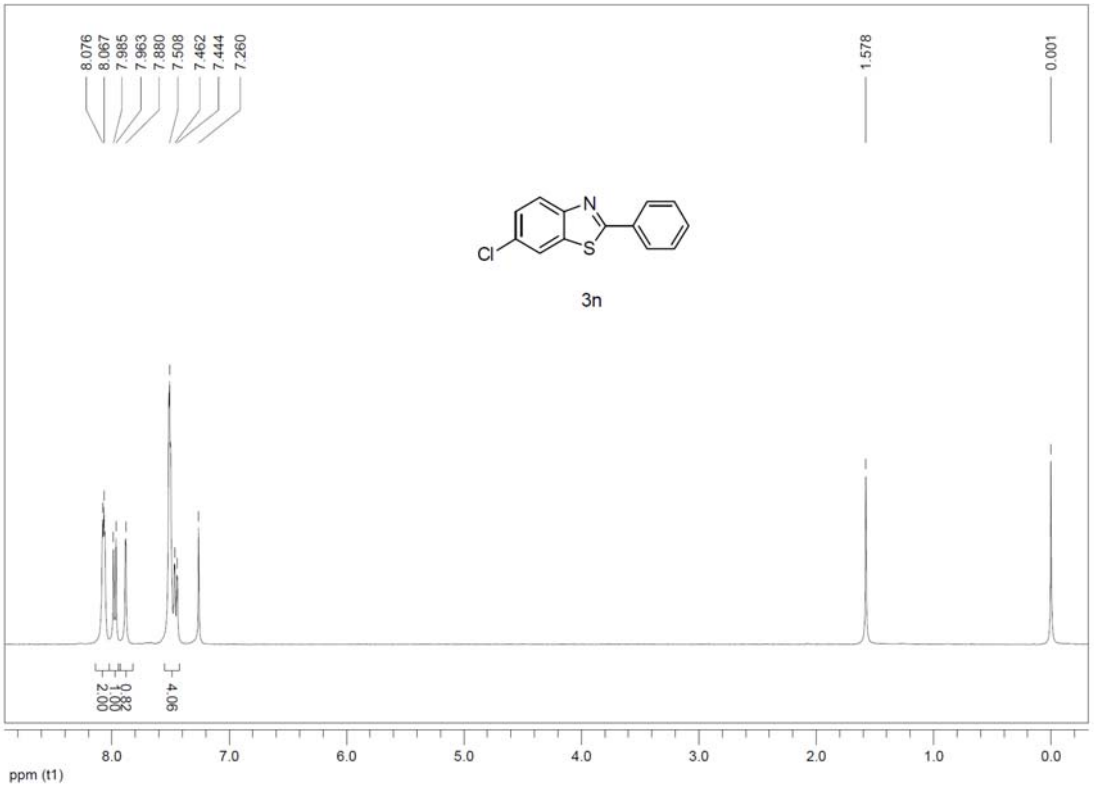
134.725
129.203
128.517
127.968
126.372
125.177
122.981
121.393
77.318
77.000
76.682
3K
150
100
50
0
ppm (t1)

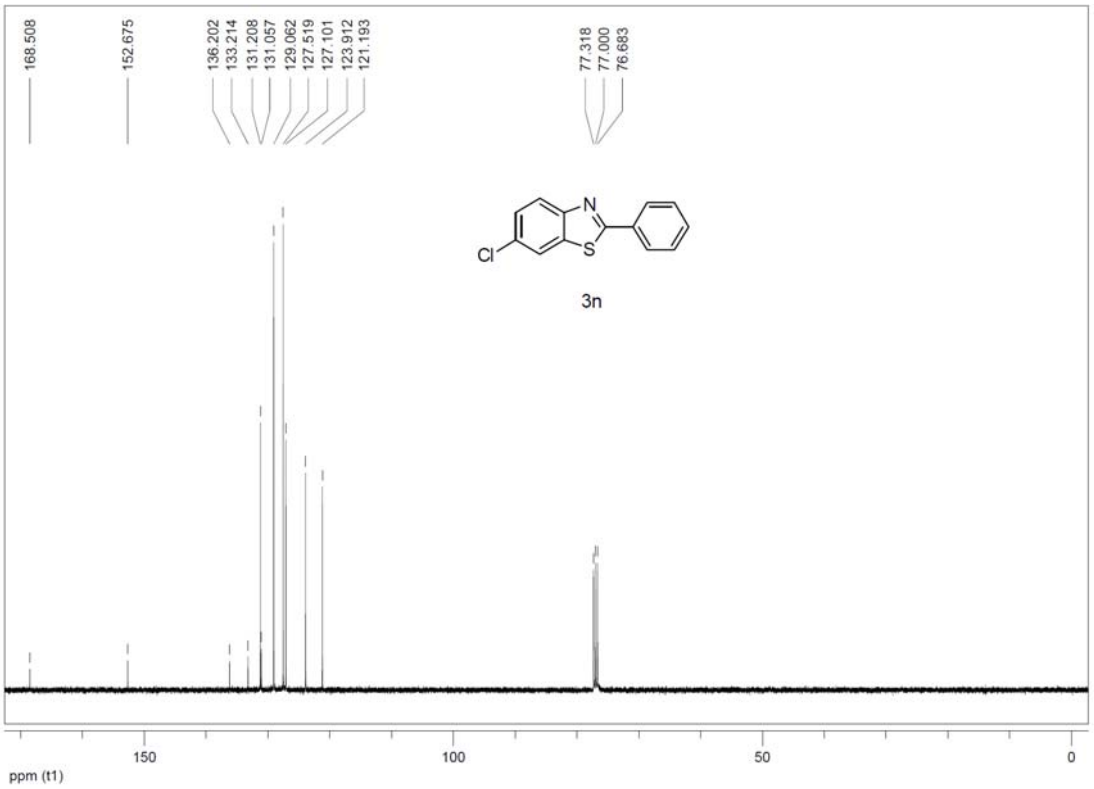

8.078
8.069
7.963
7.942
7.699
7.491
7.482
7.315
7.294
7.260
2.503
1.597
0.001
3l
2.01
1.00
1.02
3.10
1.07
3.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

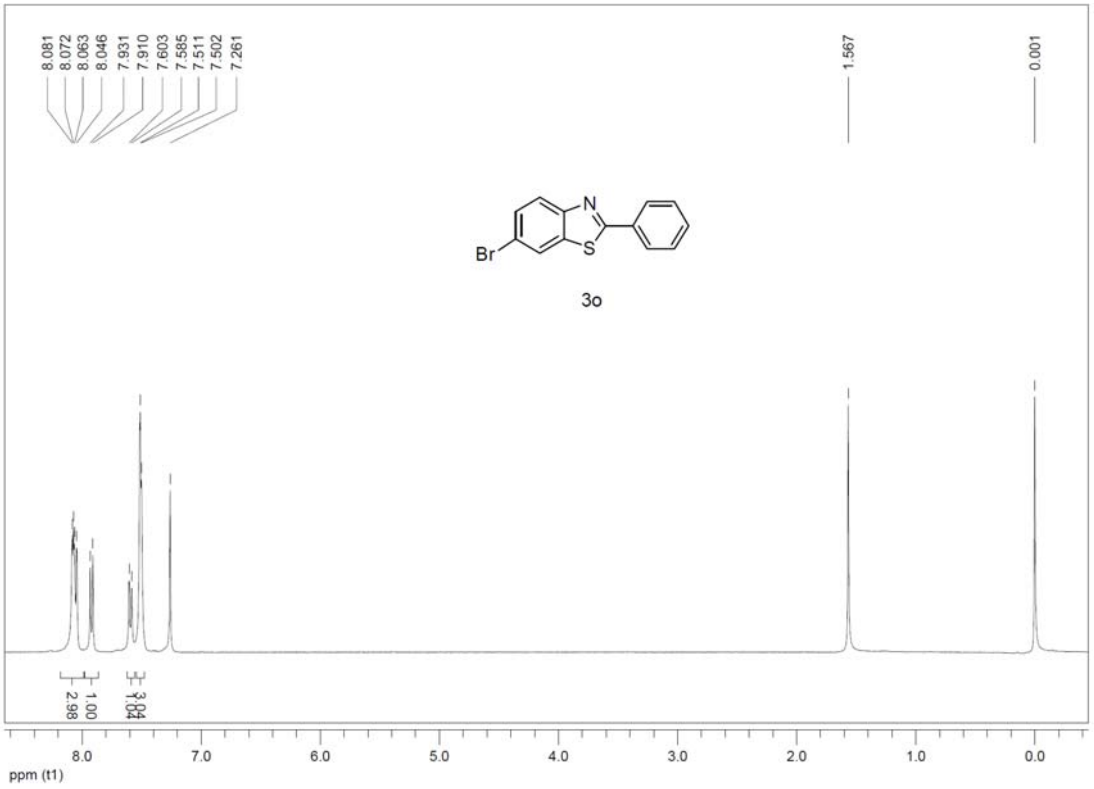

166.971
152.252
135.316
135.203
133.740
130.700
128.935
127.876
127.395
122.690
121.327
77.318
77.000
76.683
21.503
3l
150
100
50
0
ppm (t1)

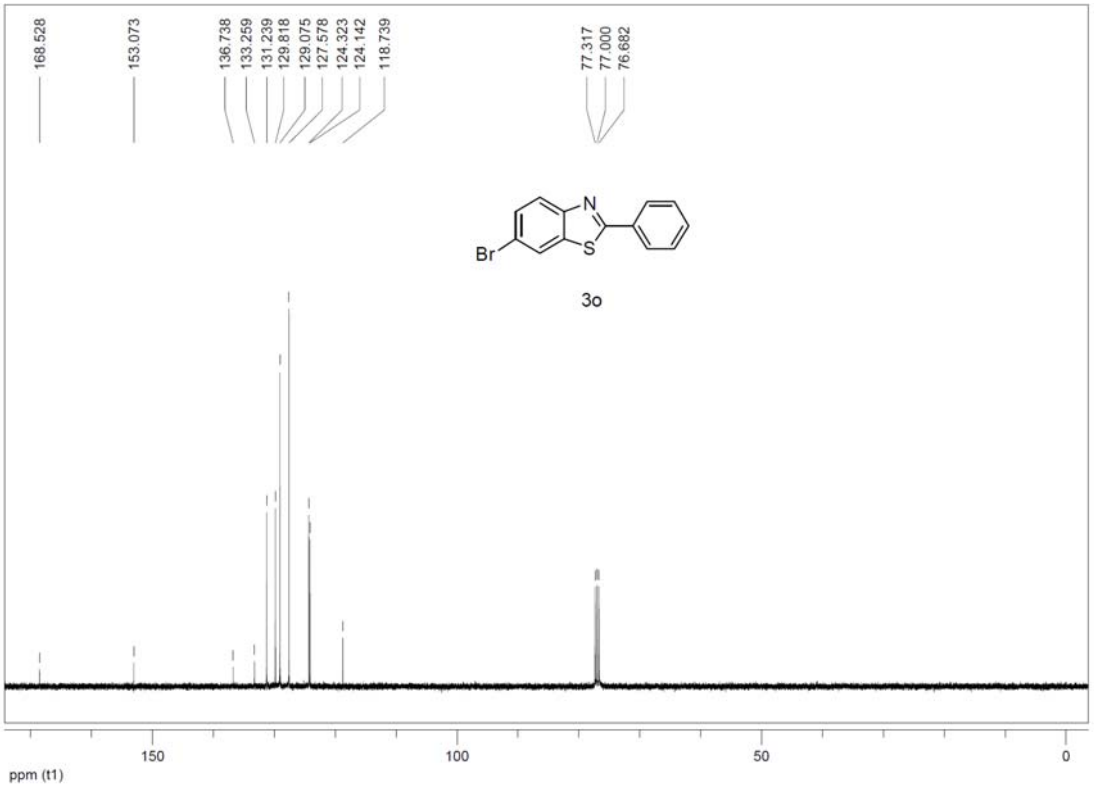

8.051
8.038
7.966
7.944
7.486
7.472
7.361
7.260
7.110
7.088
3.899
1.574
0.001
3m
2.01
1.00
3.02
1.20
1.02
3.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

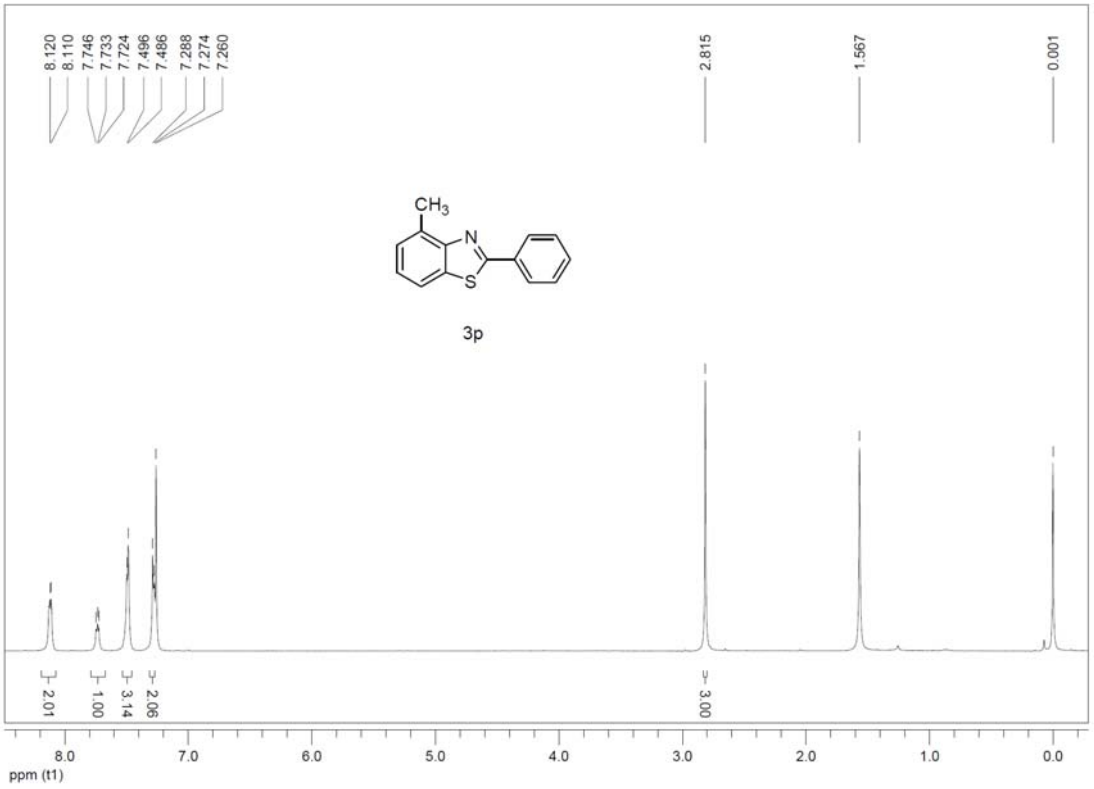

165.523
157.762
148.697
136.411
133.750
130.497
128.938
127.213
123.699
115.603
104.154
77.318
77.000
76.683
55.766
3m
150
100
50
0
ppm (t1)

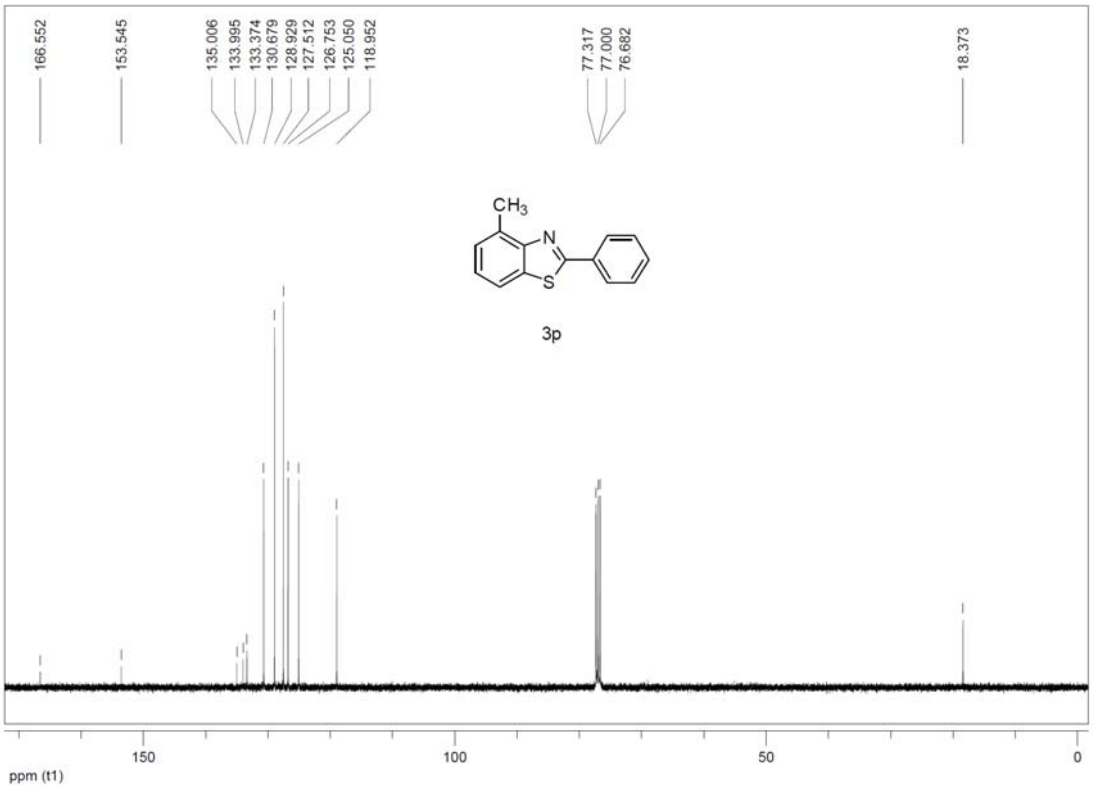

8.076
8.067
7.985
7.963
7.880
7.508
7.462
7.444
7.260
1.578
0.001
Cl
N
S
3n
2.00
2.00
1.00
2.80
4.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

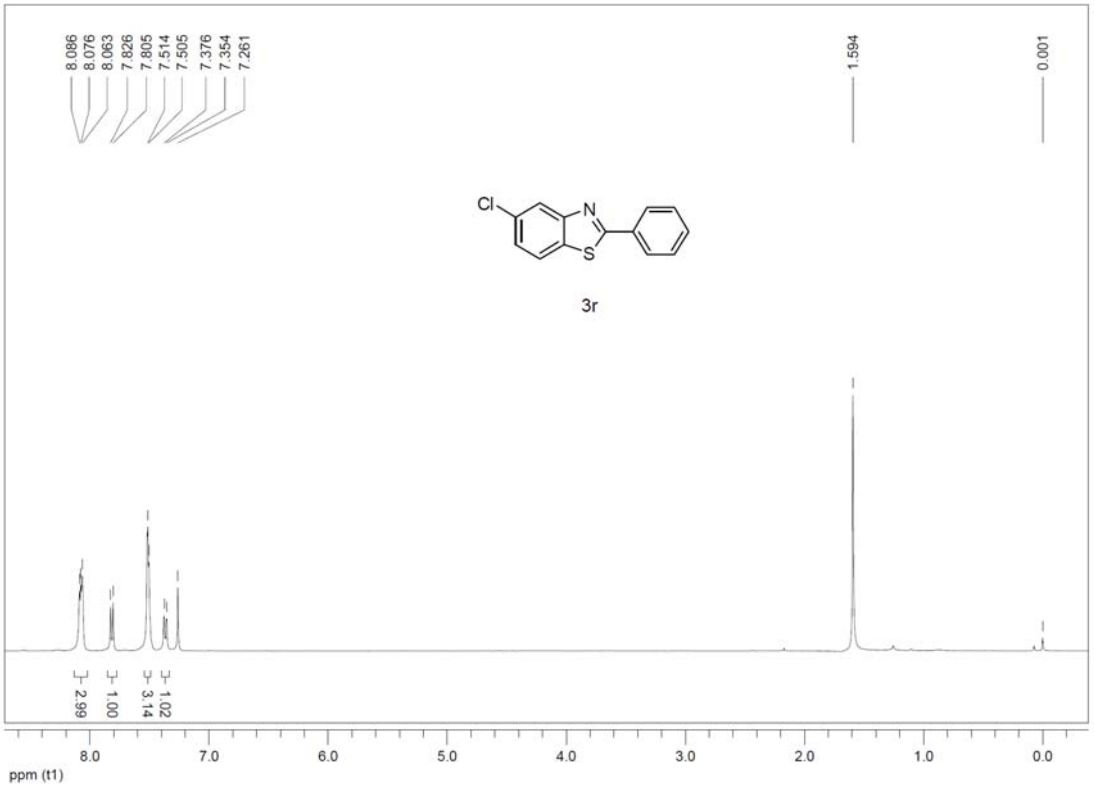

168.508
152.675
136.202
133.214
131.208
131.057
129.062
127.519
127.101
123.912
121.193
77.318
77.000
76.683
Cl
N
S
3n
150
100
50
0
ppm (t1)

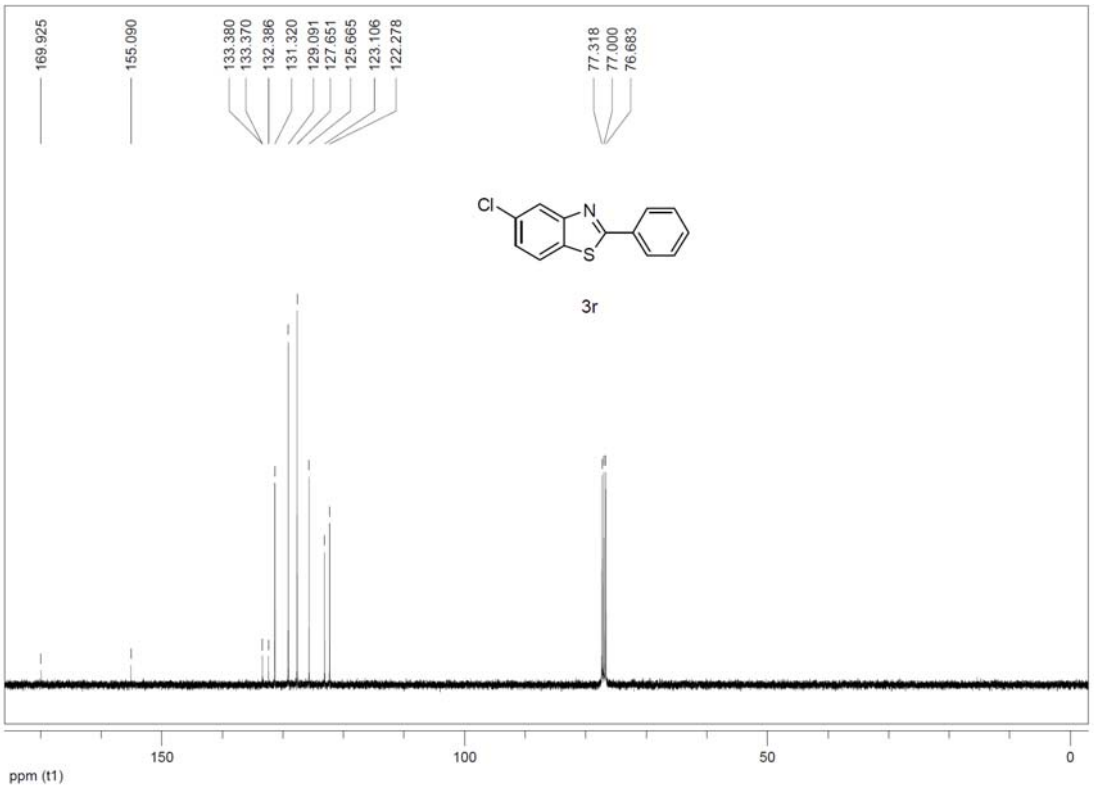

8.081
8.072
8.063
8.046
7.931
7.910
7.603
7.585
7.511
7.502
7.261
1.567
0.001
Br
N
S
3o
2.98
1.00
4.44
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

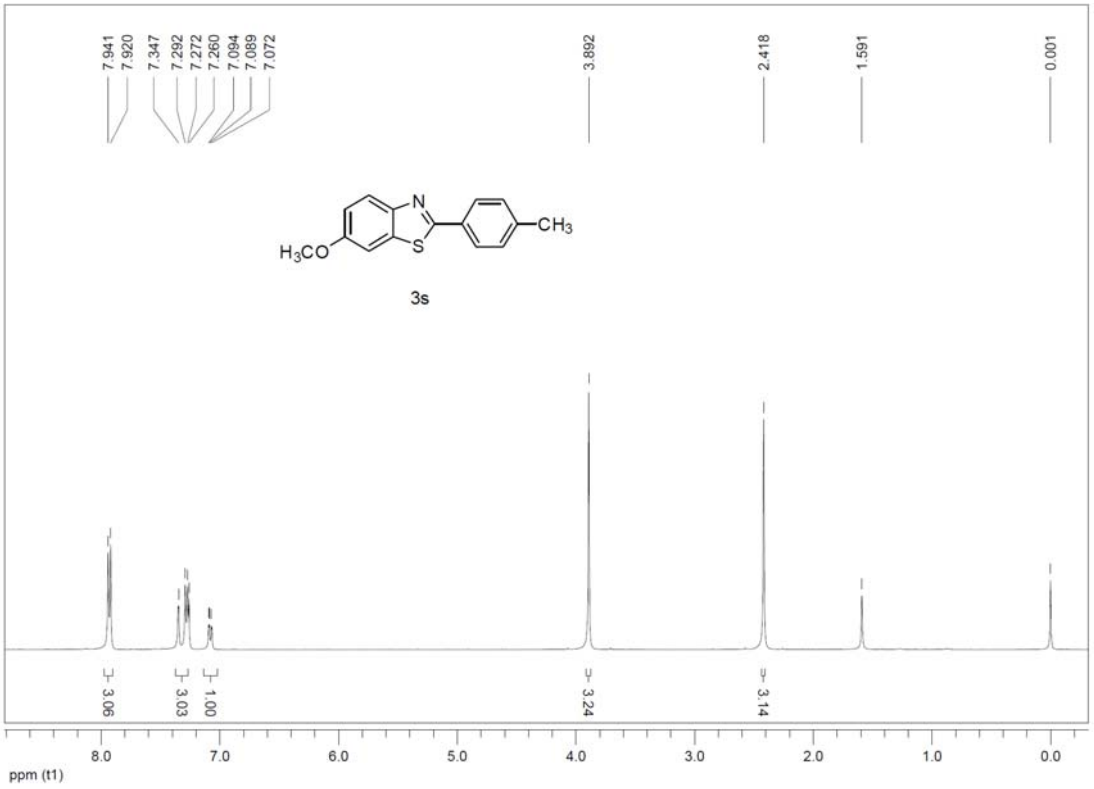

168.528
153.073
136.738
133.259
131.239
129.818
129.075
127.578
124.323
124.142
118.739
77.317
77.000
76.682
Br
N
S
3o
150
100
50
0
ppm (t1)

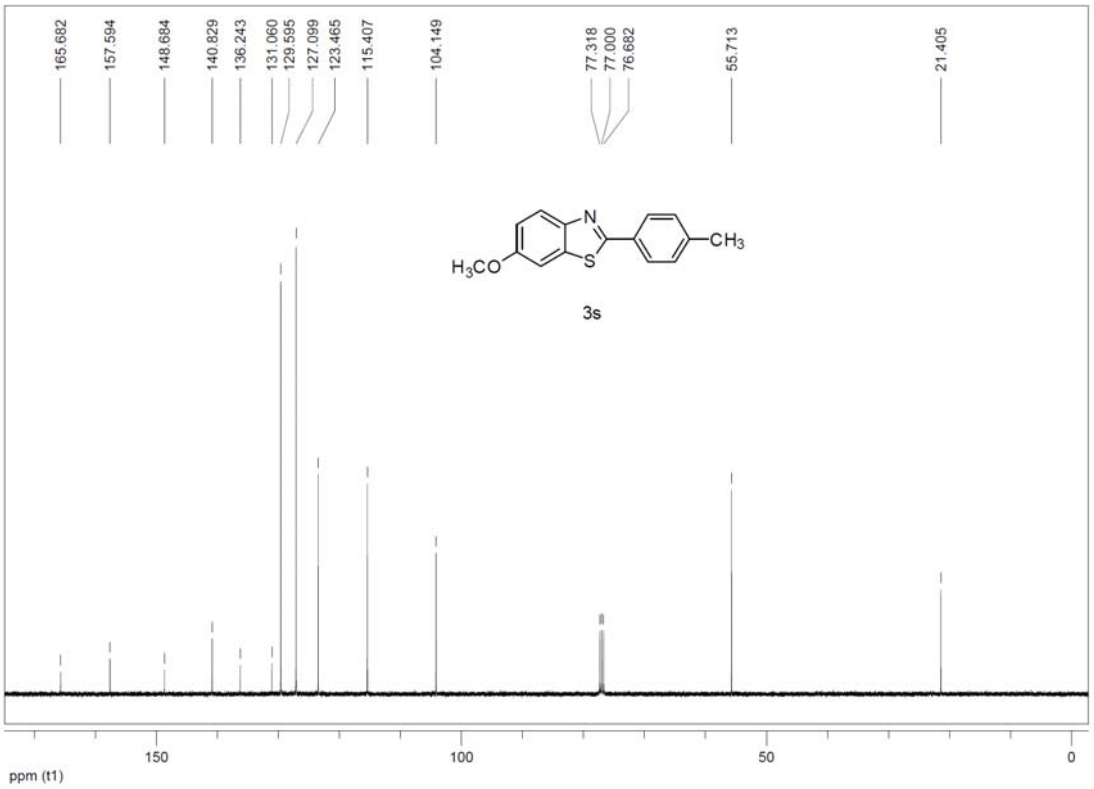

8.120
8.110
7.746
7.733
7.724
7.496
7.486
7.288
7.274
7.260
2.815
1.567
0.001
CH3
N
S
3p
2.01
1.00
3.14
2.06
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

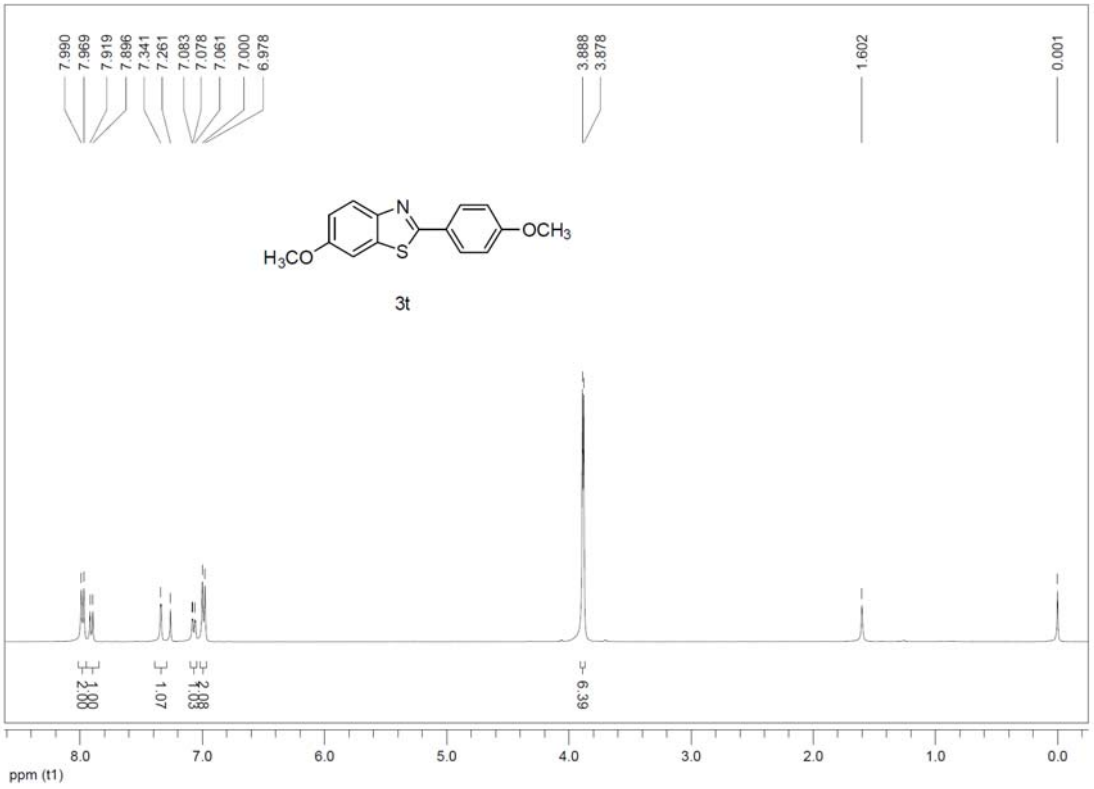

166.552
153.545
135.006
133.995
133.374
130.679
128.929
127.512
126.753
125.050
118.952
77.317
77.000
76.682
18.373
CH3
N
S
3p
150
100
50
0
ppm (t1)

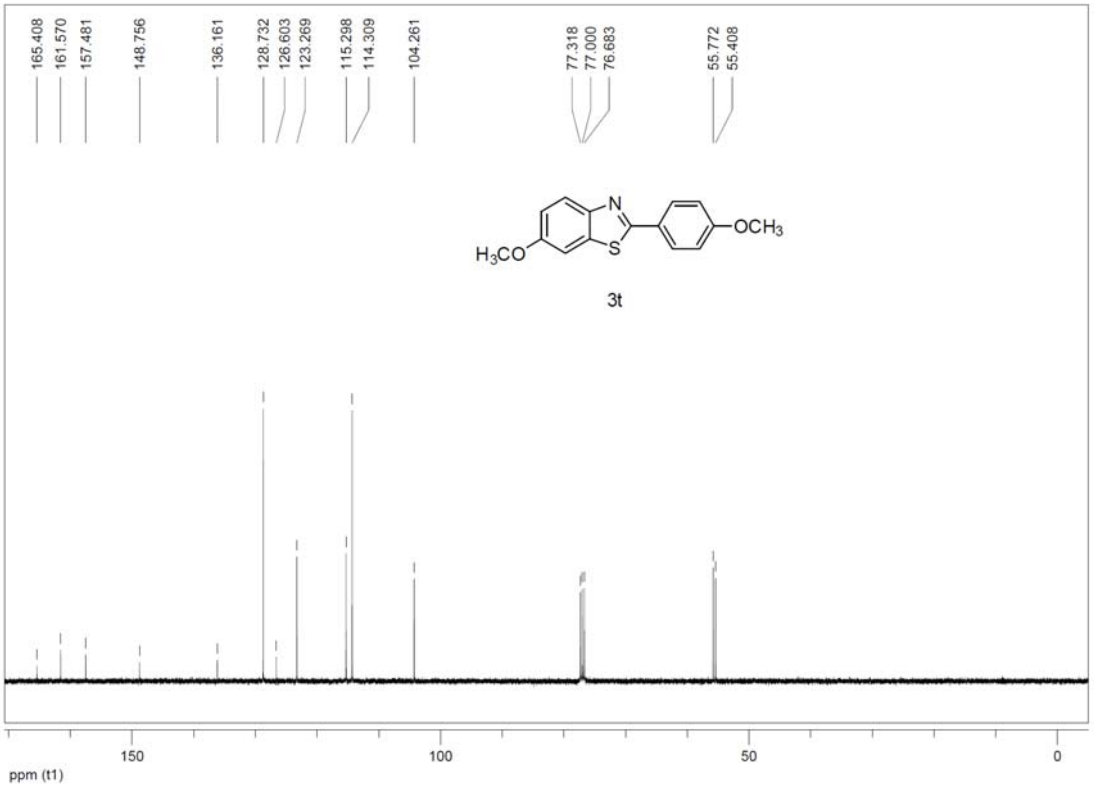

8.086
8.076
8.063
7.826
7.805
7.514
7.505
7.376
7.354
7.261
1.594
0.001
Cl
N
S
3r
2.99
1.00
3.14
1.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

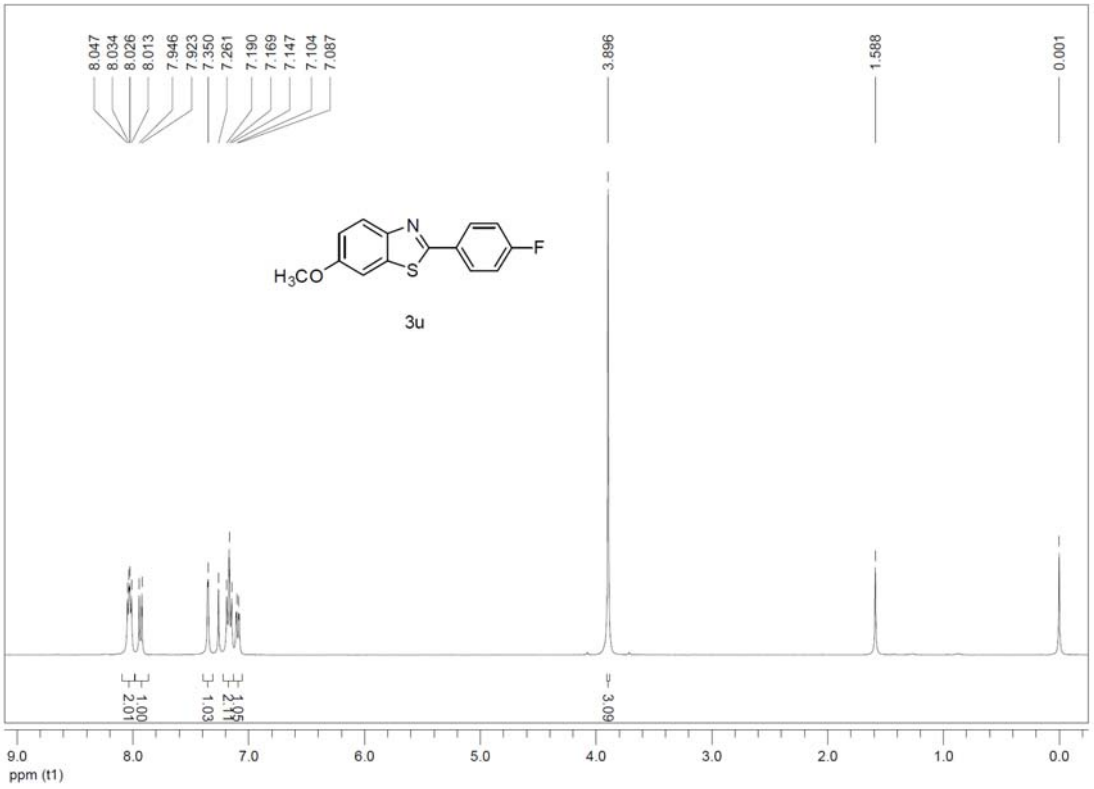

169.925
155.090
133.380
133.370
132.386
131.320
129.091
127.651
125.665
123.106
122.278
77.318
77.000
76.683
Cl
N
S
3r
150
100
50
0
ppm (t1)

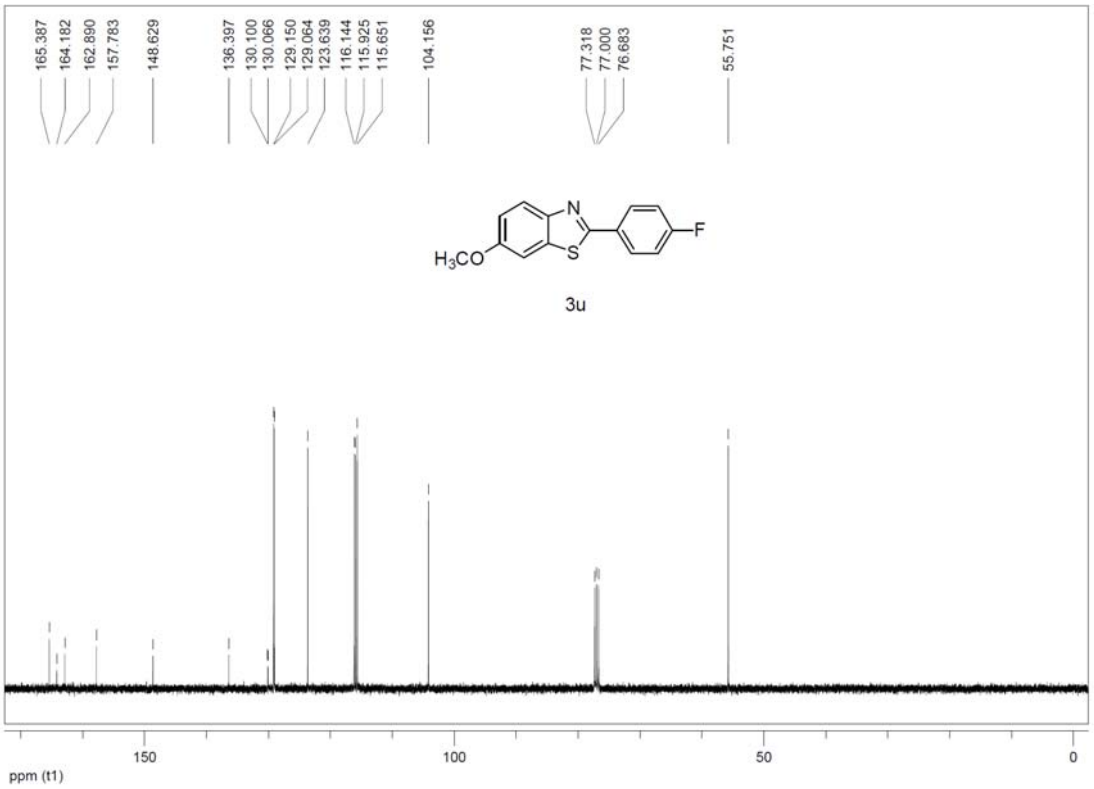

7.941
7.920
7.347
7.292
7.272
7.260
7.094
7.089
7.072
3.892
2.418
1.591
0.001
3s
3.06
3.03
1.00
3.24
3.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

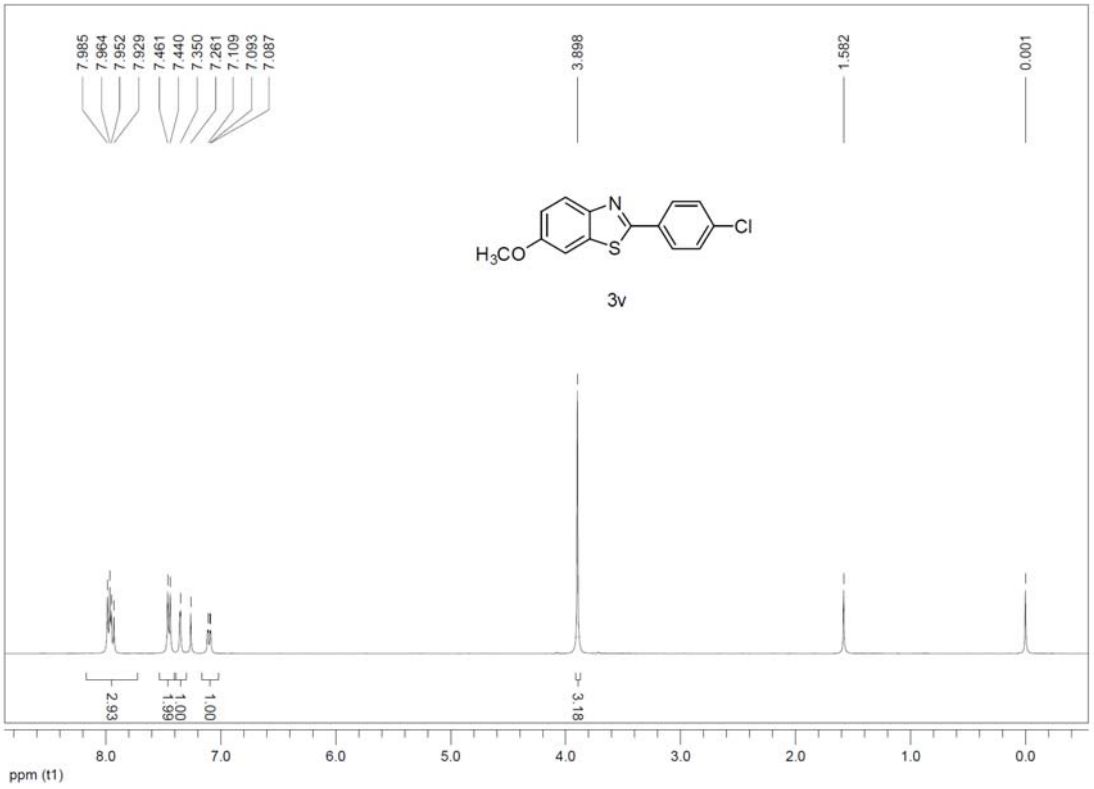

165.682
157.594
148.684
140.829
136.243
131.060
129.595
127.099
123.465
115.407
104.149
77.318
77.000
76.682
55.713
21.405
3s
150
100
50
0
ppm (t1)

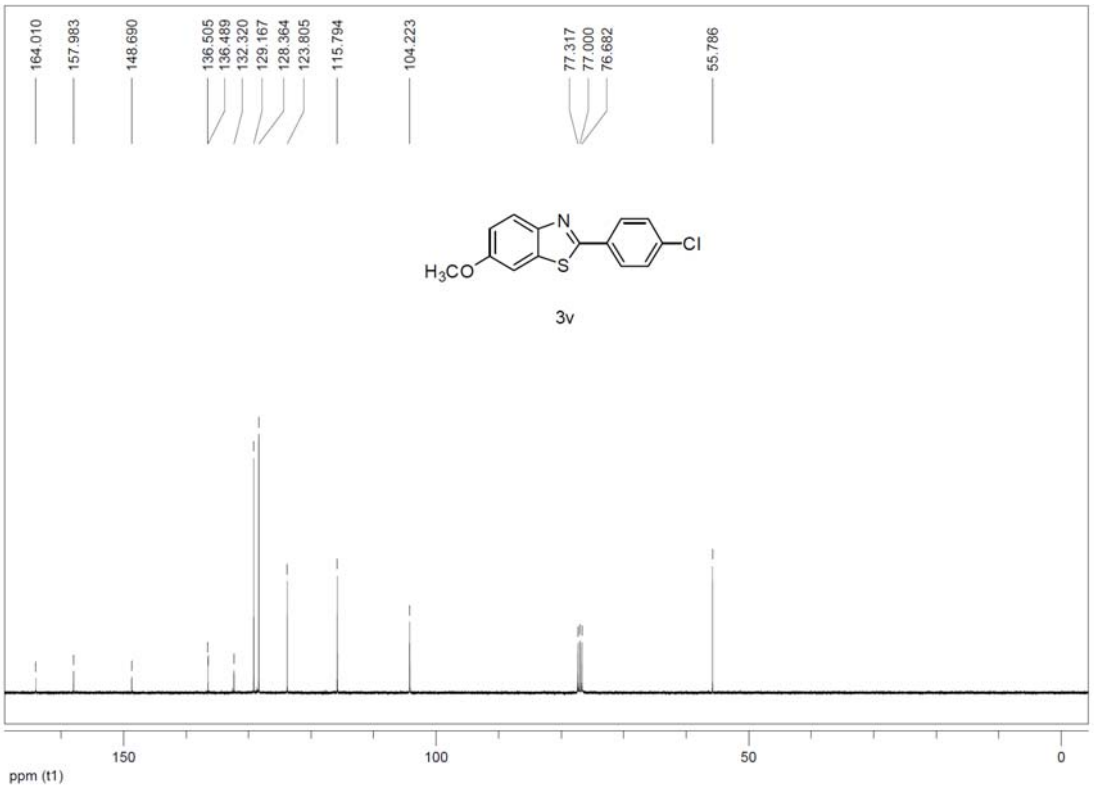

7.990
7.969
7.919
7.896
7.341
7.261
7.083
7.078
7.061
7.000
6.978
3.888
3.878
1.602
0.001
N
S
H3CO
OCH3
3t
2.00
1.07
2.08
6.39
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


165.408
161.570
157.481
148.756
136.161
128.732
126.603
123.269
115.298
114.309
104.261
77.318
77.000
76.683
55.772
55.408
N
S
H3CO
OCH3
3t
150
100
50
0
ppm (t1)


8.047
8.034
8.026
8.013
7.946
7.923
7.350
7.261
7.190
7.169
7.147
7.104
7.087
3.896
1.588
0.001
3u
2.01
1.00
1.03
2.11
1.05
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

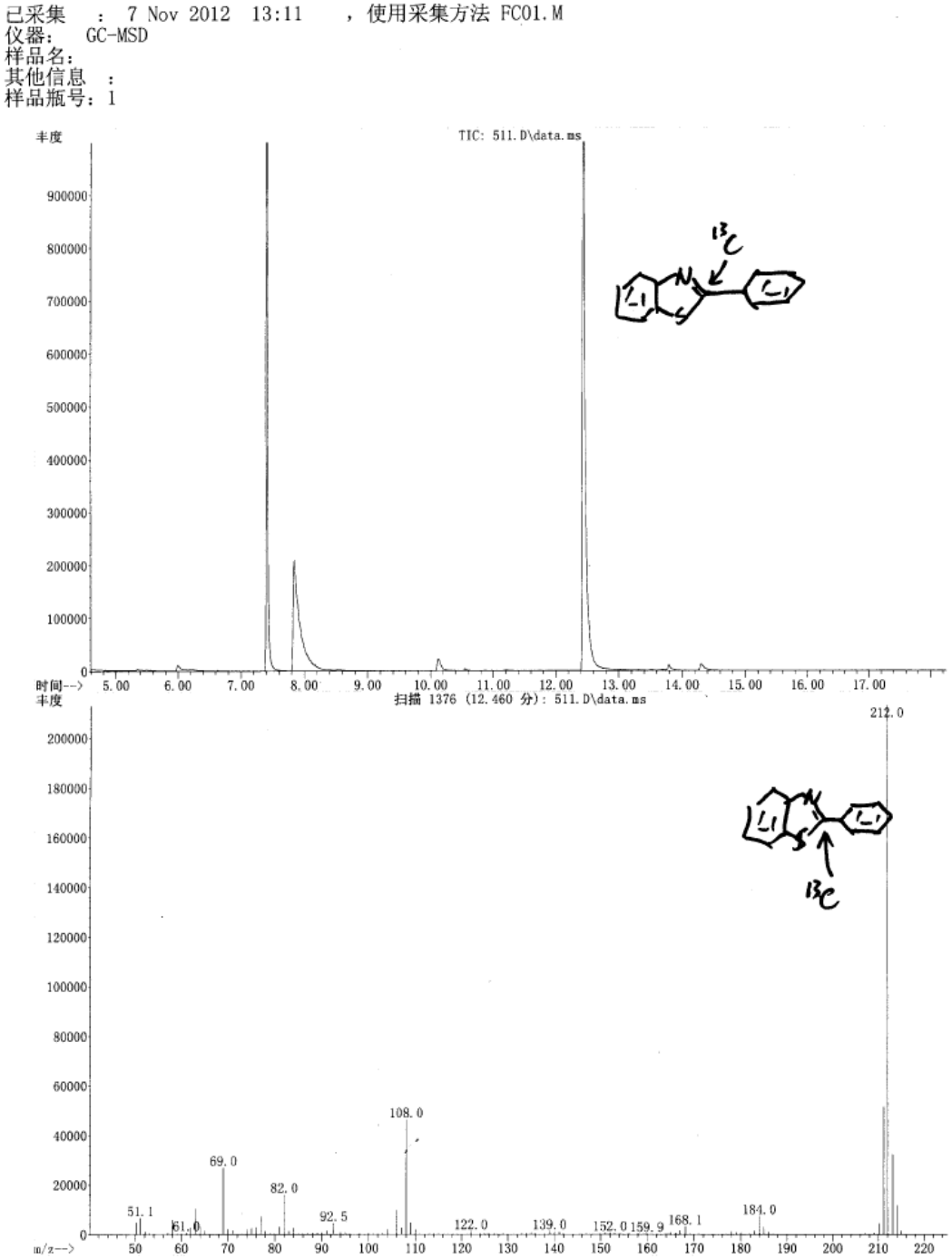

165.387
164.182
162.890
157.783
148.629
136.397
130.100
130.066
129.150
129.064
123.639
116.144
115.925
115.651
104.156
77.318
77.000
76.683
55.751
3u
150
100
50
0
ppm (t1)


7.985
7.964
7.952
7.929
7.461
7.440
7.350
7.261
7.109
7.093
7.087
3.898
1.582
0.001
N
S
Cl
H3CO
3v
2.93
1.99
1.00
1.00
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

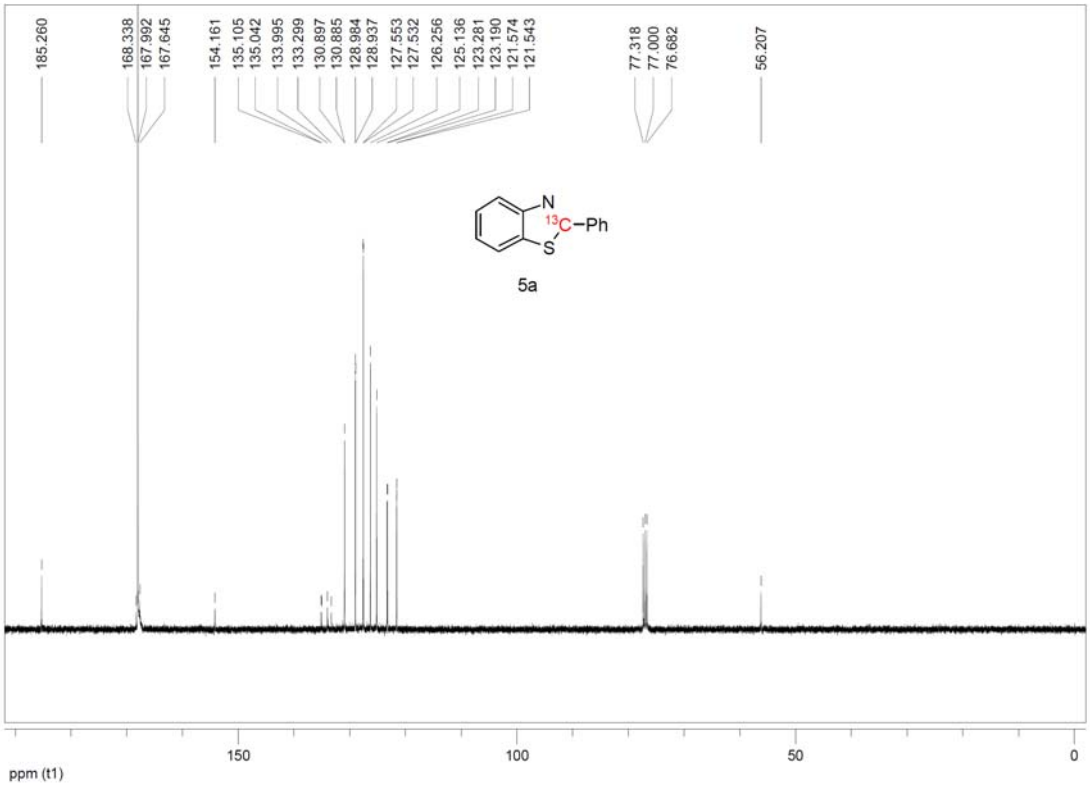

164.010
157.983
148.690
136.505
136.489
132.320
129.167
128.364
123.805
115.794
104.223
77.317
77.000
76.682
55.786
N
S
Cl
H3CO
3v
150
100
50
0
ppm (t1)

GC-MS and ^{13}C NMR for ^{13}C labeling reaction

GC-MS:



^{13}C NMR:


185.260
168.338
167.992
167.645
154.161
135.105
135.042
133.995
133.299
130.897
130.885
128.984
128.937
127.553
127.532
126.256
125.136
123.281
123.190
121.574
121.543
77.318
77.000
76.682
56.207
N
13C–Ph
S
5a
150
100
50
0
ppm (t1)